SINTERING

by

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The results of experimental and theoretical investigations of the sintering process in crystalline solids are reviewed in a primarily pedagogical manner. Emphasis is placed on elucidating the origin of the driving force for the process and the mass flow mechanisms controlling sintering so as to establish a logical basis for understanding the effects of various parameters on densification kinetics. In this respect, the effects of the aggregation of powder particles in the unsintered compact, grain growth during sintering, and reducing the average particle size in the starting powder, are discussed in detail. The essential features of theoretical models of initial, intermediate, and final stage sintering are outlined; and the degree to which these models are successful in predicting the course of the process is discussed.
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SINTERING*

J. E. Burke and J. H. Rosolowski

1. INTRODUCTION

In modern technical terminology the term "sintering" is used to describe the phenomena which occur when useful solid products are made from inorganic powders—either metallic or nonmetallic. The process is relatively easily accomplished. An array of particles of suitable size (commonly a few microns or less in diameter) is heated to a temperature between 1/2 and 3/4 of the absolute melting point for times of the order of one hour. During this treatment the particles join together, the piece shrinks, and much of the void volume which resulted from the initial misfit of the powder particles is eliminated.

It was originally thought that a liquid phase had to be present to accomplish the consolidation, and in its early use the term had this connotation (etymologically "sinter" and "cinder" are the same word). It is now recognized that particles that are solid at all times can be joined by sintering both in the presence and absence of a liquid phase is technologically important, and the term is used to refer to both processes indiscriminately. Cobalt-cemented tungsten carbide for tool bits and 95% alumina ceramics for electronic applications are examples of liquid phase assisted sintering. Tungsten metal and uranium dioxide for nuclear fuel elements are each consolidated by sintering without a liquid phase.

The phenomenon of sintering has interested scientists and technologists for many years, and a great number of papers have been written describing various aspects of the process. From a scientific standpoint the goal has been to establish the driving force, the mechanisms of matter transport, and the kinetics of the processes that lead to particle joining and porosity elimination. In part, the approach has been to mathematically model the process to permit the derivation of expressions that will predict the kinetics of shrinkage as a function of the important variables such as diffusion coefficient, particle size, etc.

A second motivation for sintering research has been to establish the factors which influence processing times and temperatures, and the structure and properties of the final product. Here powder characteristics and preparation, the presence of additives and liquid phases, the firing atmosphere, and pressure applied during sintering may be important. Most of these latter studies are technologically motivated.

In this review we shall treat both aspects of the problem. In the first part we shall describe the current understanding of the mechanism and driving forces of the process including some background science, and outline the important variables that influence both the rate of sintering and the structure of the final product. We shall emphasize the fact that there are many complexities to the process, and attempt to simplify them by describing the individual phenomena which may occur.

In the second part we shall outline the general approaches that have been used to formulate the kinetics of sintering more analytically in terms of models. The complexity of the process in real materials makes it impossible that such approaches can lead to a universal quantitative expression to describe the course of sintering in a real material. However, such studies do permit verification of the mechanisms we shall merely stipulate in the first part of this report, and hence have been the subject of extensive and useful work.

We shall not at all cover certain important technological aspects of the process such as powder preparation, fugitive binders, pressing procedures, or furnace construction and operation.

2. SINTERING OF POWDERED METALS AND CERAMICS

Sintering is the fundamental fabrication process in both powder metallurgy and ceramics, but there are important differences which stem from the differences in the nature of the materials. Powder metallurgists are most interested in the phenomenon of particle joining, since a compact of moderate strength can be plastically deformed and heat treated to control the final product. Brittle ceramics cannot be treated in this way, and the porosity and grain size present at the end of the sintering operation are those that appear in the final product. As a result, ceramists have focused most attention on powder compact shrinkage, pore elimination, and grain growth.

The application of the science and technology of sintering has become more sophisticated. In recent years it has been used to make alloys of properties and compositions not attainable by more conventional means. Ceramics have been produced by conventional cold press and sinter techniques in which the residual porosity is less than 1 part per million.

3. PHENOMENOLOGICAL DESCRIPTION OF SINTERING IN THE ABSENCE OF A LIQUID PHASE

3.1 Particle Joining

When two particles are placed in contact and heated to an appropriate temperature, they bond
Fig. 1 Neck growth between spheres without mutual approach of centers. No shrinkage occurs.

Fig. 2 Neck growth between spheres with mutual approach of centers. Shrinkage occurs.

together, and with continued heating a measurable neck will form between them. Figure 1 shows that neck growth may occur by transport of matter from the particle surfaces to the re-entrant region between them while retaining the separation between the centers of the original particles. This could occur by an evaporation-condensation mechanism or by surface diffusion upon the particles. Repeated over many particles in a compact, this process will produce particle joining, but no shrinkage.

Figure 2 shows the joining of particles with the mutual approach of centers. In principle this can occur by plastic flow much as two particles of modeling clay can be pressed together, or by various volume diffusion processes, in which matter in the region of overlap between the spheres is transported to the neck region by diffusional transport of individual atoms or ions through the bulk of the material or along the grain boundary that must appear at the contact between the two differently oriented crystalline particles.

Kuczynski(1, 2) analyzed the kinetics of neck growth between metal particles, and deduced from his analyses and supporting experimental observations that the major operational mechanism of matter transport is solid-state diffusion. The process involves the diffusional transport of atoms from the vicinity of grain boundaries to the neck region or to the pore that develops in the later stages of sintering. It is frequently convenient to describe this process in terms of a flow of lattice vacancies that are transported from the neck or pore to the grain boundary, where they are annihilated. The pore is thus the vacancy source and the grain boundary the vacancy sink. Kuczynski adopted this method of describing matter flow, and his analysis—as well as other more recent ones—will be discussed in more detail later.

3.2 Sintering Temperature

It is common, particularly in technological work, to speak of a "sintering temperature." In practice, the term refers to that temperature at which the desired amount of consolidation can be accomplished in reasonable periods—usually of the order of a few hours. For the particles of the order of 1 μ in diameter which are commonly used in ceramic work, a reasonable sintering temperature is approximately 0.75 of the absolute melting point.

Since the process is controlled by solid-state diffusion, it is also possible to define the temperature in terms of the diffusion coefficient for the slower moving species. Results from the few cases where diffusion data are available indicate that with a starting particle size of about 1 μ and a diffusion coefficient of $10^{-12}$ cm$^2$/sec, the sintering time is about 1 hour.

4. THE DRIVING FORCE FOR SINTERING

It is self-evident that sintering, being a spontaneous process, is accompanied by a decrease in the free energy of the specimen. Most workers consider the driving force to arise from the tendency of a powder compact to reduce its solid-vapor surface area, and hence to reduce the total surface free energy. A few have postulated that the driving force arises from the tendency to release the energy stored in the particles (as dislocations and elastic stresses) from prior deformation. Finally, it is possible that a driving force might result from gradients in chemical composition that are produced during sintering, or transformations to a more stable crystalline phase. In this section we shall discuss surface free energy as the origin of the driving force because it is overwhelmingly the most important factor. This will be followed by a brief consideration of the other factors.

4.1 The Kelvin Equation

It is convenient to set forth at this point some basic relationships about surface energy.

We may define the surface energy of a liquid-vapor interface, $\gamma_{lv}$, as
\[ \gamma_{lv} = \frac{dG}{dA} \]  

(1)

where \( G \) is the total free energy of the liquid and \( A \) is the surface area. Now assume a body of liquid of molal volume \( V \) and with a flat exposed surface, and a small droplet of radius \( h \) which contains \( n \) moles of liquid. The difference in the molal free energy between the two bodies of liquid is \( \Delta G \), the vapor pressure in equilibrium with the flat surface is \( P_0 \), and that in equilibrium with the droplet is \( P \).

Let us now evaporate \( dn \) moles of vapor from the droplet and condense it on the flat liquid surface. The initial volume of the droplet is \( nV = \frac{4\pi r^3}{3} \) where \( v \) is molar volume.

The free energy change in the droplet from the transport of \( dn \) moles of liquid from it is

\[ dG = \Delta G dn = \gamma_{lv} dA \]

(2)

But \( n = \frac{4\pi r^3}{3v} \) and \( dn = \frac{4\pi r^2 dr}{v} \),

\[ A = \frac{4\pi r^2}{} \]  
and \( dA = 8\pi r dr \);

hence \( \Delta G = 2\gamma_{lv} v/r \).

(3)

Since from a well-known thermodynamic relationship we may also write the difference in chemical potentials, \( \mu \), of atoms in the vapor over the two surfaces as

\[ \mu_1 - \mu_0 = \Delta G = RT \ln(P/P_0), \]

(4)

we see that

\[ \frac{2\gamma_{lv} v}{r} = RT \ln(P/P_0). \]

(5)

This relationship between surface curvature, surface energy, and equilibrium vapor pressure was first formulated by Lord Kelvin, and is commonly called the Kelvin equation. It applies equally to describe the way that the vapor pressure of a droplet or small solid sphere increases with decreasing size, to describe the increasing solubility with decreasing particle size, and even to give the concentration of lattice vacancies in equilibrium with a spherical void or pore in a solid. This latter example is of extreme importance in the formulation of pore elimination rates.

The application of this equation to the change in free energy associated with the transport of matter to or from a curved surface is standard. It is less generally appreciated that this relationship applies equally well to particles of any arbitrary shape. There is an excess free energy associated with the existence of a surface, and since all atoms in the volume bounded by that surface are in equilibrium with it, they all share in this excess free energy. It makes no difference whether the particle is a cube, a sphere, or any other shape.

This is readily shown by repeating the argument above for a solid cube of side \( h \), having a surface energy given by \( \gamma_{sv} \). In that case

\[ n = h^2/v, \]

\[ dn = \frac{3h^3}{v} dh, \]

\[ A = 6h^2, \]

\[ dA = 12 hdh, \]

and

\[ \Delta G = \frac{\gamma_{sv} dA}{dn} = \frac{4\gamma_{sv} v}{h}; \]

which is equivalent to the expression already derived for a sphere.

In many cases, it is convenient to use the Kelvin equation in somewhat modified form. Letting \( \Delta P = P - P_0 \), then \( P/P_0 = (P_0 + \Delta P)/P_0 = 1 + \Delta P/P_0 \) For values of \( x \) less than 0.1, \( \ln(1+x) = x \) within 5%. Hence we may write Eq. (5) as

\[ \Delta P = P_0 \left( \frac{2\gamma_{sv} v}{rRT} \right). \]

(6)

This approximation will not be valid for large values of \( \Delta P \), but it is easily shown that it is valid down to the smallest particle size of practical importance.

For example, in aluminum oxide we may assume some reasonable values:

\[ \gamma = 2000 \text{ dynes/cm} \]

\[ v = \text{molecular wt/density} = 25.4 \]

\[ R = 8.3 \times 10^7 \text{ ergs/deg-mole} \]

\[ T = 2000^\circ \text{ Kelvin} \]

then \( r = 6 \times 10^{-6} \text{ cm} \), or about 0.1\mu diameter, which is approximately the lower size limit of particles used in sintering.

4.2 Curvatures in Three Dimensions

In two dimensions, curvature can be simply expressed by stating the radius of curvature. In a three-dimensional body, it is necessary to specify the radius of curvature of the surface as observed in two orthogonal planes, and the net curvature, \( 1/r \), is

\[ \frac{1}{r} = \left( \frac{1}{r_1} + \frac{1}{r_2} \right). \]

In a sphere, \( r_1 = r_2 \) and

\[ \frac{1}{r} = \frac{2}{r_1} \].
In a cylinder, \( r_2 = \infty \) and
\[
\frac{1}{r} \neq \frac{1}{r_1}.
\]
In saddle-shaped bodies, \( r_1 \) and \( r_2 \) have different signs, and if \( r_1 = -r_2 \), \( r = \infty \), and the net curvature is zero.

4.3 Application to Particle Joining and Pore Elimination

The difference in the chemical potential that has been shown to exist between spherical particles of different sizes also exists between regions of different curvature on the same surface. Referring to Fig. 3, one may therefore say that the vapor pressure over the hill is greater than that over the flat surface by an amount
\[
P = P_0 \left(\frac{2\gamma_{sv} \sqrt{Y}}{rRT}\right),
\]
where \( \gamma_{sv} \) is the solid-vapor surface energy. The valley shown in the figure has a curvature of negative sign, and hence
\[
P = -P_0 \left(\frac{2\gamma_{sv} \sqrt{Y}}{rRT}\right).
\]

For the totally enclosed pore, it is more convenient to think of the relative concentrations of the lattice vacancies in equilibrium with the pore and the flat surface, and for a pore of radius \( r \)
\[
C = C_0 \left(\frac{2\gamma_{sv} \sqrt{Y}}{rRT}\right),
\]
where \( C_0 \) is the vacancy concentration beneath the flat surface.

Hence, in all cases there will exist between

\[
\text{Fig. 3 Structural and topographical features of a solid between which a driving force for transfer of matter exists.}
\]

\[
\text{Fig. 4 Generalized pore at a 3-grain junction when } \gamma_{gb} < \frac{1}{3} \gamma_{sv}
\]

surfaces of different curvature (or other characteristic dimension if the particles or perturbations are idiomorphic crystals in shape) a difference in chemical potential that can be reduced if matter is transported from the small to the large particle, or from the convex to the concave portion of the surface. This is the origin of the driving force that acts to transport matter into the neck between particles in contact and join them together as shown in Figs. 1 and 2. In this process, the total solid-vapor surface area is reduced.

4.4 Importance of Grain Boundary Energy

In the above discussion, the fact that differently oriented crystalline particles will be separated by a grain boundary when they join is ignored. However, the energy expended to form this grain boundary must be subtracted from the energy associated with solid-vapor interface decrease which occurs during sintering when calculating the total free energy change for the process.

Figure 4 shows a generalized pore which has formed by the sintering of particles, and the particles are now separated by boundaries of energy \( \gamma_{gb} \). (The two-dimensional case shown may be considered to be a cross section of a tubular pore intersected by three-grain boundary planes. Somewhat more complicated relationships exist in an isolated pore at a four-grain junction, but they are qualitatively similar and we shall not consider them here.)

The angle made by the pore-grain boundary intersection is the same as at a grain boundary groove,
\[
\cos(\theta/2) = \gamma_{gb} / 2\gamma_{sv}.
\]
pore resulting from pore surface elimination is $6Y_g/vX$ and the energy increase resulting from the formation of new grain boundary is $6Y_gb/nX/3$. But since when $8 = 60^\circ$, $Y_gb = \sqrt[3]{3} Y_{sv}$, and these energies just balance. Thus for this configuration there is no net driving force for sintering. The general conclusion is that pores which have concave sides (when viewed from within the pore) will shrink. Pores which have convex sides, such as shown in Fig. 6, will grow. Substantially all pores ever observed in solids have concave sides; but, in principle, grain boundary energy can be high enough to produce convex pores, and perhaps they do appear in such substances as silicon carbide.

In general, for almost all materials $Y_gb$ is considerably less than $Y_{sv}$, and the pores on grain boundaries are more or less spherical. As Prochaza(3) has suggested most elegantly, however, it may well be that those peculiar solids which sinter only with great difficulty, such as silicon carbide, are ones in which $Y_gb > \sqrt[3]{3} Y_{sv}$.

4.5 Powder Activity

Some powders sinter better than others. There are many reasons for this—relatively simple by themselves—but most complex in combination. The prediction of the sintering behavior of a powder from a few simple laboratory measurements has proved to be most difficult, and for technologists in particular has led to surrounding the whole area of powder characterization with an aura of mystery. The terms "powder activity" or "powder sinterability" are commonly used when these baffling behaviors are encountered. In this section we shall discuss some of the reasons for the obscure observations.

4.5.1 End Point Density and Sintering Rate

One major difficulty lies in the inexact description of what is meant by "better" sintering. As has been indicated, a high total surface energy generally results in a high driving force for sintering, and the major mechanism of matter transport is volume diffusion, so small particles should sinter "better" (faster or at lower temperatures) than coarse ones both because there is more surface area per unit volume and because transport distances are shorter.

Most scientific studies of sintering involve at least the measurement of the rate of shrinkage of specimens up to a shrinkage of several percent. Figure 7 illustrates schematically a typical observation. A shrinkage law of the type

$$\frac{\Delta L}{L_0} = kt^n$$

is commonly observed during the initial stage of sintering, where $L_0$ is the initial magnitude of some linear dimension of the powder compact, $\Delta L$ is the change in that dimension, and $t$ is time. The exponent $n$ ranges from 1/3 to 1/2 and $k$ is proportional to the cube of the particle radius.

Fig. 5 Pore at a 3-grain junction when $Y_gb = \sqrt[3]{3} Y_{sv}$.

Fig. 6 Pore at a 3-grain junction when $Y_gb > \sqrt[3]{3} Y_{sv}$.

Referring now to Fig. 5, $Q$ will be $60^\circ$ and the pore will have straight sides when $\cos(\theta/2) = 3/2$ and $Y_gb = \sqrt[3]{3} Y_{sv}$.

Suppose under these circumstances the pore shrinks from the size $ABC$ to the size shown by the dotted lines $A'B'C'$. Each side of the pore will be shortened by $2X$, and each grain boundary will be lengthened by $C-C'$, which a little geometry will show is $2X/\sqrt{3}$.

Now the free energy decrease per unit length of
relationships are consistent with those obtained from analysis of theoretical models of the process as will be described later.

If powder activity is measured by the initial sintering kinetics, it will be universally observed that a fine powder sinters faster than a coarse one. From a technological standpoint, however, the more important parameter is the ultimate density obtained in the sintered piece. "Better" sintering means a higher density product. As is illustrated schematically in Fig. 8, sintering commonly ceases, for practical purposes, before all pores are eliminated, and theoretical density is attained. An example of such "permanent" residual porosity is shown in Fig. 14E. There are a number of reasons why such residual porosity is observed, but they are not in general related to particle size. As a result, if sintering is continued long enough, it is quite possible to attain a higher density in a specimen made from a coarse powder than in a specimen made from a fine powder.

It is obvious that, if density of the sintered piece after a given sintering treatment is the criterion of powder "activity," the selection of the more active powder may depend on the sintering time. In the example given in Fig. 8, the fine powder yields a more dense specimen than the coarse one after 2 to 3 hours of sintering, but the coarse powder will yield a more dense product after about 24 hours of sintering.

4.5.2 Surface Area as a Measure of Powder Activity

Simple instruments are now commonly used to measure the surface area of a powder by the Brunauer-Emmet-Teller or similar techniques involving the adsorption of a gas on the surface of powder particles, and such measurements are commonly taken to be a measure of powder activity.

To some extent they are, but even though the tendency to reduce a high total surface energy is the predominant motivation for matter transport in sintering, the mere existence of a high surface area in a powder does not mean that the atom movements associated with the reduction of surface area which will occur during heating will contribute to the shrinkage process and pore elimination.

If the particles are substantially spherical in shape and uniform in size, then a surface area measurement will provide a reasonably accurate measure of particle size. As is illustrated in Fig. 2, matter transport will occur almost exclusively from the region between spheres to the region of the neck, and there will be a relatively simple relationship between powder surface area and initial sintering kinetics.

Most powders, however, do not consist of individual spherical particles. The surfaces may be rough, for example, on a scale small compared to the particle diameter. Consider the sintering of the two rough-surfaced spheres illustrated in Fig. 9. There, surface area will be much greater than that of smooth spheres of equivalent volume. The initial contact between asperities will place curvatures of small radius in contact, and some neck formation will occur at a rapid rate controlled by this small radius. However, localized matter transport that does not contribute to neck formation will also occur to smooth out the hills and valleys on the surface, as was illustrated in Fig. 3, and soon the sintering rate will be characteristic of that of spheres of the full diameter.

We conclude that the dimensions of the particle are the critical factor controlling sintering kinetics, and that, as is observed, powder surface area measurements are not necessarily a good measure of particle dimensions.

4.5.3 Particle Aggregation

Powders are commonly thought of as assemblages
The pores formed between aggregates of particles are generally larger than the pores formed between the particles in an aggregate. Proportional to $2\gamma_{SV}/r_p$, where $r_p$ is the radius of the pore. In addition, the volume needed to fill the pore is greater. For both of these reasons, and others as well, large pores between aggregate particles can be eliminated only with difficulty and will persist in the final piece.

As a consequence powders will sinter "better"; i.e., to a higher density, if they contain no persistent articles during the early aggregates that do not break down during pressing.

4.5.4 Gas Entrapment in Pores

An obvious but sometimes overlooked cause of residual porosity in sintered materials is the entrapment of insoluble gas in closed pores. During the terminal stages of sintering the pores, which originated from the misfit of the initial particles, close, and no longer communicate with the free surface. These closed pores will contain the gas which was present in the furnace atmosphere when closure occurred.

If a vacuum furnace is used, or if the furnace atmosphere is a gas that can readily diffuse through the substance being sintered, as hydrogen does through aluminum oxide, then subsequent pore shrinkage is not retarded. If the gas does not diffuse--as nitrogen does not through aluminum oxide--then pore shrinkage will be inhibited. As the pore shrinks past the size at the time of pore closure, the pressure inside the pore will ultimately reach the pressure that can be imposed by the surface tension of the material and
When the surface of the substance is thus balanced by the internal pressure of the pore, there is no longer any action for sintering.

The importance of entrapped insoluble gas in is commonly neglected in most scientific studies of sintering, but it is a very important technological consideration for residual porosity in sintered materials.

Residual Stresses in Powder Particles

It is commonly observed that grinding powders in a mill will yield a higher density product, although the surface area as measured by conventional gas adsorption is little altered. Such powders are freely termed to be "active." Some authors argue that improved sintering behavior (higher final density) results from an increase in driving force because elastic energy is stored in the particles during grinding. There is no evidence to indicate that the amount of energy that can be stored in this way effectively increase the rate of sintering. In atomic mobility is by definition high at the sintering temperature and the elastic stresses and dislocations must be removed by slight atom movements of annihilation of dislocations in times short relative to those required to accomplish much more sinterable.

Energy storage from paracrystalline solid is probably much higher than pores which lie near grain boundaries. However, all pores originate misfit between the original particles of the aggregate caused by grinding do not appreciably increase the rate of sintering. Energy storage from paracrystalline solid is probably much higher than those required to accomplish much more sinterable.

Rain Growth During Sintering

It was stated earlier, and will be discussed in detail later, that the elementary process in sintering is the transport of lattice vacancies from one to the grain boundaries in the polycrystalline solid where they are annihilated. It is further observed that pores which lie on grain boundaries disappear much more rapidly than pores which lie near the surface of grains. However, all pores originate from the grain boundaries and some grain boundary or pore movement have occurred if pores are observed inside.

This section we shall discuss the phenomena of growth, grain boundary movement, pore-grain interaction and breakaway, and their control importance to the sintering process.

Particle Growth During the Early Stages of Sintering

Analysis of the sintering process attribute importance to the particle sizes in the powder.
one to another three-grain intersection line. It is convenient to represent grains in a solid by a two-
dimensional figure such as Fig. 11; however, it should be remembered that the structure shown is really a
section through a three-dimensional grain array.

At suitable temperatures, grain boundaries can move readily in solids. The general observation is
that they move toward their center of curvature, as indicated by the arrows in Fig. 11, at a rate given by:

\[ V = MP \]

where \( V \) is the velocity, \( M \) the mobility, and \( P \) the driving force.

The driving force, \( P \), is proportional to the local curvature of the grain boundary surface and is given by

\[ P = \gamma_{gb} \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \]

and the general expression for grain boundary velocity becomes

\[ V' = M \gamma_{gb} \left( \frac{1}{r_1} + \frac{1}{r_2} \right). \]

5.2.1 Grain Growth Rate in Polycrystals

By making a large number of approximately correct assumptions, it is possible to deduce from Eq. (7) a law for "normal" grain growth in polycrystals. The most important of these assumptions are:

- The average radius of boundary curvature, \( r \), is proportional to the grain diameter \( G \).
- The grain size distribution in the piece is, except for a scale factor, independent of the average grain size.

With these, and more subtle assumptions, one may write

\[ \frac{dG}{dt} = \frac{AM \gamma_{gb}}{G}. \]

where \( A \) is a constant related to the geometry, and

\[ G^2 - G_0^2 = 2AM \gamma_{gb} t. \]

where \( G_0 \) is the grain size at \( t = 0 \). Frequently this is simplified to

\[ G = kt^n. \]

and indeed much commonly obtained grain growth data can be roughly described by this relationship: empirically, the exponent \( n \) has values of about 1/3 to 1/2 at a maximum.

Fig. 12 Geometry assumed when calculating the binding force between a spherical particle or pore and a curved grain boundary.

5.3 Interactions Between Pores or Other Inclusions and Grain Boundaries

When a grain boundary intersects an inclusion, a portion of the boundary equal to the cross-sectional area of the inclusion is eliminated. As a result, there is a binding force of the inclusion to the grain boundary, and the boundary can move only by breaking away from the inclusion or by pulling it along with it.

5.3.1 Binding Force of Pore to a Grain Boundary

The magnitude of the binding force of a pore to a boundary can be computed by reference to Fig. 12.

Let a grain boundary of surface energy \( \gamma_{gb} \) intersect a spherical inclusion of radius \( r \). In the absence of any force tending to move the boundary away from the pore it will intersect it along a great circle. If a force exists to move the inclusion in the \( y \) direction relative to the boundary, the grain boundary will move down along the sphere, always intersecting it in a radial direction as demanded by the balance of surface tension forces.

When the force is sufficient to have the grain boundary make an angle \( \theta \) with respect to the diametral plane, there will be exerted a force of \( \gamma_{gb} \) dynes/cm along the circumference of the small circle of radius \( r' = r \cos \theta \), and in the direction of the grain boundary. By resolving these force components along the \( y \) direction, the net force on the inclusion is found to be

\[ F = 2\pi \gamma_{gb} r \cos \theta \sin \theta. \]

Since \( 2 \cos \theta \sin \theta = \sin 2\theta \), which is a maximum when \( \theta = 45^\circ \), the maximum value of the force (and therefore the binding force of the pore to the boundary) is

\[ F = \pi \gamma_{gb}. \]
5.3.2 Prevention of Grain Boundary Movement

A sufficient number of immobile inclusions bound to a grain boundary having a radius of curvature \( r_k \) can prevent its movement, and in a polycrystal can prevent grain growth. This situation will obtain when the restraining force of \( n/A \) inclusions per unit area just matches the driving force \( 2\gamma_{gb}/r_k \). Using the frequently made assumption that \( f_k \) is proportional to the grain size, \( G \), and that the inclusions are spheres of radius \( r_i \), growth will stop when

\[
(n/A) r_i = 2/\pi G. \tag{13}
\]

Assuming all grains are cubes, the number of grains per unit volume is

\[
N = 1/G^3.
\]

The grain boundary area in the specimen, per cube is \( 6G^2/2 \) since each boundary is shared between two grains, and the grain boundary area per unit volume is thus

\[
A = 3/G.
\]

The number of spherical pores or inclusions per unit volume of the specimen is

\[
n = \frac{f r_i^3}{4\pi^3 / 1},
\]

where \( f \) is the volume fraction of inclusions.

Case 1: If all of these pores or inclusions lie on the grain boundaries (as is commonly the case for pores in a sintering specimen), the number of inclusions per unit area is

\[
n/A = \frac{f G}{4\pi r_i^3},
\]

and substituting for \( n/A \) in Eq. (13)

\[
f = 8(r_i/G)^2. \tag{14}
\]

If all of the assumptions made in this derivation are met, grain growth will stop when this condition is fulfilled, except for the important case of exaggerated grain growth discussed in Section 5.4.

Case 2: If the pores or inclusions are uniformly dispersed through the specimen, the number of inclusions per unit area of grain boundary will be the number found in the volume contained within a distance \( r_i \) on either side of the unit area. Thus

\[
n/A = \frac{f}{4\pi r_i^3} \cdot 2r_i = \frac{3f}{2\pi r_i^3},
\]

and substituting again in Eq. (13) yields

\[
f = \frac{4}{3}(r_i/G), \tag{15}
\]

Fig. 13 Exaggerated grain growth in Al2O3. Note preponderance of "trapped" pores inside of the larger grains.

5.3.3 A Revised Equation for Grain Growth

We earlier stated that the rate of grain growth is proportional to the driving force. We have also just shown that, in the presence of a uniform array of inclusions, the driving force arising from the curvature of the grain boundary can be diminished by an amount up to

\[
\frac{n}{A} r_i \gamma_{gb},
\]

which will lead to a termination of grain growth at a grain size that can be found from Eq. (14) or (15).

Calling this limiting grain size \( G_e \), we may then revise the grain growth equation [Eq. (9)] to read

\[
\frac{dG}{dt} = AM_{gb} \left( \frac{1}{G} - \frac{1}{G_e} \right);
\]

a relationship first obtained by Burke. (5)

5.4 Exaggerated Grain Growth

The preceding discussion has been concerned exclusively with so-called "normal grain growth," in which the average grain size gradually increases, but the grain size distribution remains constant. It is frequently observed in polycrystalline solids that some grains discontinuously grow much larger than their neighbors, a phenomenon variously called
exaggerated grain growth, runaway grain growth, secondary recrystallization, and by many other names. An example in sintered Al₂O₃ is shown in Fig. 13.

This phenomenon is of great importance in sintering, because it is accompanied by the isolation of pores inside grains, and these isolated pores substantially cannot be removed by subsequent heat treatment. Techniques for the inhibition of such exaggerated grain growth have been developed for a few materials, and have permitted ceramics to be sintered to nearly theoretical density. Some of the understanding of these phenomena will be presented in this section.

5.4.1 Conditions for Exaggerated Grain Growth

In Section 5.3 it was shown that grain boundary motion stops when the restraint of immobile inclusions just matches the driving force provided by the curved boundary. (In fact, it can be shown that when this condition obtains, a boundary which is curved on a macroscopic scale has no net curvature when the regions surrounding each pinning particle are examined in detail.) Two invalid assumptions are made in that discussion, however. The first is that the curvature of all boundaries in a polycrystal are the same, and in fact that is not so. The second is that the pores or dislocations pinning the boundaries are immobile--there is ample evidence that they can move under the stress imposed by the boundary.

Assume that both these invalid assumptions hold--then no grain boundary can move. Now, assume that one grain boundary is free to move, because its radius of curvature is smaller than that of the other boundaries. This boundary will then pull away from the pinning inclusions (or pores) and some grain growth will occur locally. As the growing grain adds sides, the curvature of its boundaries will become more pronounced, so that it is even more able to consume its neighbors. Under these circumstances, the phenomenon of exaggerated grain growth occurs, during which the rapidly moving grain boundaries break away from pores on them, thus leaving the pores inside the grains. Practically, these pores are never eliminated and the consequence to sintering is that the attainment of a pore-free product is impossible.

5.5 Pore-Free Products From Sintering

In a few cases of technological importance it has been found possible to inhibit exaggerated grain growth, and thereby permit sintering to proceed to the point of virtually complete pore elimination. The technique has involved making small additions of other substances to the powder.

The production of almost pore-free aluminum oxide is one of the most striking examples of the use of this technique. This material has a very high light transmitting ability and is currently used as the envelope material for high-pressure, high-temperature sodium discharge lamps such as the Lucalox® lamp. In this case the additive is about 0.1% of MgO.

An even more impressive example is the ceramic Yttralox®--in which about 10 mole percent of thorium oxide is added to yttrium oxide powder. This material, unlike alumina, has a cubic crystal structure and hence is optically isotropic. The product is transparent, and residual porosities as low as 1% per million have been achieved by careful processing.

The additives that promote sintering are commonly called "grain growth inhibitors" or "sintering aids." In fact, however, considerable grain growth may occur during sintering of powders doped with them, and the time and temperature needed to attain 95% of theoretical density is about the same in specimens made from pure powder as it is in specimens made from doped powder. What the additives do is to inhibit exaggerated grain growth. Grain boundaries therefore do not pull away from pores and entrap them inside grains as they do in ceramics made from the pure powders.

In the rest of this section we shall present the current understanding of the mechanism by which such additives permit the attainment of theoretical density in a sintered ceramic.

5.5.1 Pore Mobility

In the preceding discussions on grain growth and pore-grain boundary interactions it was assumed that pores in solids could not move. In fact, there is considerable evidence that pores can, and do move under the pull of a grain boundary. Movement can occur by diffusion on the surface of the pore, or by transport of vapor across the pore. The laws governing pore mobility depend upon the transport mechanism; but, in general, the mobility increases with decreasing pore size, and more quantitative calculations indicate that the mobility should be inversely proportional to some low power of the pore diameter.

5.5.2 Pore-Grain Boundary Separation

In Section 5.3.2 we set forth the conditions for the grain boundary curvature necessary to permit a boundary to separate from a pore. Basically the requirement was that the curvature of the boundary be great enough to overcome the binding force of the immobile pores on the boundary.

If, however, we consider the additional fact that the pores are mobile, then the condition for breakaway is drastically changed. Indeed, if the mobility of the pores is great enough to permit them to keep up with the boundary, they will remain there as grain growth occurs and will eventually be eliminated through shrinkage.

Briefly, we can then say that if the pores, in response to the forces exerted upon them by the grain boundaries, can achieve a velocity equal to that achieved by the boundaries acting in response to all the forces exerted upon them, then exaggerated grain growth will not occur. Pores will remain on boundaries, and it will be possible to sinter to theoretical density.
We may thus conclude that exaggerated grain growth will not occur if the pore and boundary velocities, \( V_B \) and \( V_B \), are related by

\[
V_B = M_B P_B = M_B P_B = V_P,
\]

where \( M_B \), \( M_P \), \( P_B \), and \( P_P \) are the mobilities and driving forces for the movement of the boundaries and pores, respectively.

The values of \( P_B \), \( P_P \), and \( M_B \) are controlled in a given material by the curvature of the boundary and the radius of the pore. However, there is good evidence that the mobility of a boundary can be markedly reduced by the adsorption of a second constituent upon it. (8, 9) In a pure substance, grain boundary mobility can be exceedingly high, and we interpret the common occurrence of exaggerated grain growth in most ceramics to the fact that \( V_B \) exceeds \( V_P \).

We similarly attribute the inhibition of exaggerated grain growth in magnesia-doped alumina and thoria-doped yttria to the reduction of grain boundary mobility in those materials by the additives. The conditions of Eq. (16) are thus fulfilled, and sintering to nearly theoretical density is possible because most pores remain on grain boundaries.

As yet, there is no good theory to guide the selection of exaggerated grain growth inhibitors, such as MgO in Al₂O₃. Those that have been found to be effective have been empirically discovered.

6. OTHER SINTERING MODES

6.1 Liquid Phase Sintering

Sintering with the presence of some liquid phase that wets the solid is a technologically important process since it occurs in the production of many ceramic wares, such as chinaware and porcelain enamels. It is also important in the sintering of a number of powder metallurgy products. The sintering process passes through one or two stages depending on the relative amounts of liquid and solid phase present, and whether or not the solid can dissolve in the liquid. A liquid that does not wet the solid has no effect on, or will inhibit, sintering.

In the first stage of such sintering, the liquid insinuates itself between the solid particles thus separating them with a lubricating film. At the same time the meniscus of liquid on each particle exerts a traction tendency to pull them together. The result is that the particles rearrange by sliding so as to reduce the porosity of the piece by improving their packing. If the quantity of liquid present is so great, or if it wets the solid so well, that most of the particles are completely covered leaving the pores bounded by the liquid, then the driving force for sintering arises from the surface tension of the liquid on the pore surfaces which tends to collapse them. In either case this stage proceeds by a viscous flow process and may result in a pore free piece if the amount of liquid present is sufficient to fill all of the original porosity. Shrinkage in this stage is usually quite rapid.

If there is some porosity remaining at the end of this first, rearrangement stage, then sintering will continue to proceed rapidly if the solid is to some degree soluble in the liquid. In that case, matter is transported from particle to particle by diffusion through the liquid. The mechanism of matter transport is that of dissolution and re-precipitation with the driving force arising from the increasing solubility of portions of the solid surface with decreasing radius of curvature, as given by the Kelvin equation. This results in the shrinkage of the small particles and the growth of the larger ones as well as the disappearance of all sharp corners, which produces a characteristic structure of rounded grains surrounded by a liquid. Shrinkage in this stage proceeds rapidly because of the high atomic diffusion coefficients in liquids.

If there is little or no solubility of the solid in the liquid then, at the conclusion of the first stage, sintering will proceed in a manner similar to that which would occur if no liquid were present. The densification rate in that case is much smaller than for the second stage described above.

A more complete discussion of the kinetics of liquid phase sintering is given by Kingery. (10)

6.2 Hot Pressing

Hot pressing is the term used to describe the process of sintering under the simultaneous influence of heat and pressure. The pressure applied is usually of the order of a few thousand psi. It is generally accepted that densification during hot pressing occurs primarily by diffusion processes, as in ordinary sintering. Plastic flow only plays a role at very high temperatures and/or pressures, or in materials with low yield strengths.

The technological advantage of hot pressing over ordinary sintering lies in the fact that by adding pressure, the elastic stress at interparticle contacts is greatly increased and so, therefore, the driving force for sintering. This occurs without a concomitant increase in the driving force for grain growth. Thus, a high density and fine grain size, otherwise impossible to attain by conventional sintering, can often be achieved by hot pressing.

A more complete discussion of this process is given by Vasilios and Spriggs. (11)

6.3 Reaction Sintering

Reaction sintering is a process of some technological importance, in which particle joining occurs with substantially no shrinkage. It is perhaps best described by a single example. Relatively strong bodies of silicon nitride (Si₃N₄) can be made by
forming the desired shapes of powdered elementary silicon and firing these at a suitable temperature in an atmosphere of nitrogen. The silicon is transformed to silicon nitride in this process, and the crystallites of the newly formed phase are strongly bonded to each other. Substantially no shrinkage occurs in this process, and obviously silicon transport occurs only for distances small compared to the initial particle diameter. Furthermore, the reaction will proceed only as long as the nitrogen gas has access to the particles of unreacted silicon, so that high-density products cannot be obtained.

7. THEORY OF SINTERING

7.1 Driving Force and Mechanisms

The basic objective of theoretical investigations of the sintering process has been to predict the time dependence of densification from the analysis of a model involving one or more sintering mechanisms. This objective is most often approached by deducing the sintering mechanism from a comparison of sintering kinetics with the predictions of models based on different mechanisms. There is still considerable controversy as to the degree to which the various mechanisms control densification in spite of the large amount of modeling work that has been done. This situation is due primarily to the oversimplifications inherent in the models used to describe the enormously complicated geometrical changes that occur during sintering. In what follows, we will discuss the various factors that must be considered when constructing a sintering model.

Recapitulating what has already been stated, the large surface energy of small particles provides the incentive to sintering of a powder compact. The particles join at points of contact forming necks. The growth of these necks is uninhibited in a powder of a glass because the total surface energy continues to decrease as they get larger. In a crystalline powder, however, the formation of a neck invariably generates a grain boundary. Such a neck can only grow if, in doing so, the energy decrease due to the loss of surface area exceeds the energy increase due to creation of a grain boundary area. This is generally what occurs because the grain boundary energy of a solid is typically about half as large as the surface energy. The creation of a neck results in a variation of surface stress over the particles in its vicinity and this leads to the appearance of an elastic stress in the particles. This stress affects the local chemical potential of the atoms. The gradient of this chemical potential, as described earlier in Section 4.1, is the thermodynamic force that drives sintering. The mode of matter transport that occurs in response to this force is termed the sintering mechanism.

Perhaps the most obvious mechanism is that of viscous flow. All the available evidence indicates that glasses do indeed sinter by this mechanism. In the case of crystalline solids, however, it appears to be ruled out as a significant contributor to sintering.

This conclusion is based on a number of observations including:

a. Calculations indicate that the yield strength of crystalline solids is only exceeded under exceptional circumstances as a result of surface tension alone.

b. Pores on and near grain boundaries disappear fastest, which would not be the case if the pores were collapsing as a result of viscous flow.

c. Experiments on the sintering of powders of alloys whose component elements have different self-diffusion coefficients indicate that variations in composition occur in the region of the neck.

d. In the sintering of the metal powders containing inert precipitates as markers, no precipitates are found in the neck regions after sintering occurs.

Items b, c, and d indicate that the sintering mechanism must be that of diffusion, whereby empty volume is transferred from the "interior" to the "exterior" of a piece or alternatively, matter is transferred from the exterior to fill the internal porosity.

It is, however, universally observed that there is no sample size effect on sintering; i.e., the rate of sintering of a piece is uniform throughout regardless of its size. This means that matter cannot be flowing by diffusion from the surface to fill internal porosity because such a flow would be strongly influenced by sample size and result in a large size effect. This apparent anomaly was resolved when it was recognized that the grain boundaries serve as sources of matter for filling the voids. As atoms leave the boundary to deposit on the surface of the void, the vacancies accumulating on the boundary combine to annihilate planes of atoms. The net result is that the powder particles (or grains) change their shapes in order to pack better, and consequently the sample shrinks.

The mechanism of sintering is therefore volume and/or grain boundary diffusion. The matter flow from a boundary to a nearby pore, however, is controlled not only by the boundary-pore geometry, but also by the magnitude of the matter flow from other boundaries nearby. This is a consequence of the fact that the whole piece shrinks uniformly. Any local departure from uniform shrinkage causes a stress buildup that affects the matter flow from nearby boundaries in a compensating manner.

7.2 Common Characteristics of Sintering Models

The task of deriving a sintering model is that of solving a diffusion problem. The problem is one of finding an expression for the time-dependent flow of atoms to pores from the adjacent grain boundaries.
in general, must be judged on the basis of the overall approach rather than on the strength or weakness of any one part. This has not, however, prevented considerable work being done on, and controversy about, *improvements* of portions of overall approximate treatments.

7.3 Development of Microstructure

Figure 14 illustrates the development of the microstructure of a ceramic during sintering, the quantitative prediction of which is the goal of sintering theory. The material is Al₂O₃ to which about 0.2 wt % MgO had been added to inhibit exaggerated grain growth. Figures 14A through D are scanning electron micrographs taken from a paper by Grekovich and Lay. (4) They show the progressive changes in structure from that of the unsintered powder compact in A through, respectively, 1, 2.5, and 6 minutes of sintering at 1700°C in B, C, and D. The porosity values in this sequence are 69, 60, 25 percent while the average grain (or particle) diameters are 0.30µ, 0.51µ, 0.85µ, and 1.78µ.

Figure 14E is a conventional micrograph of a polished section of this material after several hours of sintering when the porosity has been reduced to around 2 percent.

In normal sintering practice, the particle size distribution and pressing pressure would be chosen so as to give a porosity of 25 to 40 percent in the powder compact. The initially low density was chosen here, however, so as to clearly reveal the variation in structure. In particular, the local variations in powder packing and the resulting clumping of pores later on is apparent as well as the fact that considerable grain growth occurs even very early in sintering.

7.4 Sintering Stages

Attempts at modeling the sintering phenomenon have led quite naturally to the definition of sintering "stages," which divide the process into three periods wherein the constantly changing geometry and distribution of porosity are taken to be essentially constant. The first of these, in which the primary interest is in describing the growth of necks between particles, is called the initial stage. The separate particles of the compact maintain their identity during this stage and relatively little shrinkage occurs. Much more theoretical work has been done in attempting to describe this stage than any other.

The second is called the intermediate stage. In this the contacts have grown so that the initial powder particles have lost their identity and a considerable amount of grain growth occurs. The porosity is visualized as forming a network of interconnected channels lying along the grain edges. Most of the densification occurs during this stage, which is taken to last until the interconnected pore network starts to break up into small chains of closed pores on the grain edges. This technologically most important
stage of sintering is also the most complicated in its geometrical aspect.

In the final stage, the pores occur as isolated entities located either on the grain corners, or totally enclosed within grains as a result of moving grain boundaries having swept by them. A study of this stage is technologically important as it bears on the question of the ultimate practical degree to which porosity may be eliminated during sintering.

7.5 Initial Stage Sintering Models

In a now classic pair of papers, Kuczynski(1, 2) treated the kinetics of the growth of a neck between a sphere and a plane and a cylinder and a plane. He considered four mechanisms of neck growth: viscous flow, surface diffusion, evaporation-condensation, and volume diffusion. In dealing with the diffusion mechanisms, he, as well as almost all subsequent workers, found it convenient to refer to the flow of vacancies instead of the flow of atoms. The driving force for this flow was taken to be the difference between the vacancy concentration in the region just under the strongly curved neck surface and that in the rest of the system.

In a solid not subject to elastic stress, the atom fraction of vacancies present at equilibrium at a temperature T is given by

\[ C_0 = \exp \left( \frac{-E_f}{kT} \right) \tag{17} \]

where \( E_f \) is the energy required to form a vacancy and \( k \) is Boltzmann's constant. Since \( E_f \) is typically of the order of 1 ev, \( C_0 \) is always a small number even at the melting temperature. Thus the vacancies can be considered to be in dilute solution in the solid and hence their chemical potential is directly proportional to their concentration. The stress on the neck surface increases the chemical potential of the vacancies there. The neck growth process is visualized as occurring because vacancies leave the neck surface for the interior in order to achieve their equilibrium concentration, but in doing so they increase the neck radius, thus decreasing the stress and, consequently, the magnitude of the equilibrium concentration. Some of the vacancies so "freed" may then diffuse to grain boundaries and cause shrinkage to occur.

The magnitude of the equilibrium vacancy concentration under the neck is obtained by finding that concentration for which the energy increase in the solid that results from introducing a few more vacancies is just equal to the energy decrease that results from the associated increase of the radius of curvature of the neck, as calculated from the Kelvin equation. The result is that the atom fraction of vacancies under the neck surface, \( C_n \), is given by

\[ C_n = C_0 \exp \left( \frac{\gamma_{SV}}{kT r_n} \right) \tag{18} \]

where \( \gamma_{SV} \) is the vacancy volume and \( r_n \) is the radius of curvature of the neck as shown in Fig. 2. Since \( \gamma_{SV} \) in solids is generally no larger than 2000 ergs/cm\(^2\), the concentration difference is closely approximated by

\[ \Delta C = C_n - C_0 = C_0 \left( \frac{\gamma_{SV} v}{kTr_n} \right) \tag{19} \]

Kuczynski calculated his diffusive matter flows by assuming the vacancy concentration gradient at the neck could be approximated by dividing Eq. (19) by the radius of curvature of the neck, \( r_n \). The rate of change of neck volume was then expressed as

\[ \frac{dV}{dt} = D_v A \left( \frac{\Delta C}{r_n^2} \right) \tag{20} \]

where \( D_v \) is the vacancy diffusion coefficient, and \( A \) is the area through which the flow takes place. This area was taken equal to the neck area for volume diffusion and to the cross-sectional area of a cylindrical shell having internal radius \( x \) and a thickness of one lattice parameter for the case of surface diffusion. He expressed his results for all mechanisms in the general form

\[ \frac{m}{n} = \frac{x}{r} = L(T) \tag{21} \]

where \( x \) and \( r \) are the neck and sphere radii, respectively, as shown in Fig. 2; \( t \) is time; and \( L(T) \) is a temperature dependent factor. The values he obtained for \( m \) and \( n \) are given in Table I.

Kuczynski then compared his theoretical results with experimental observations made on the necks that grew as spheres of copper and silver sintered to plates of the same metal, and as silver wires sintered to a plate. He concluded that neck growth occurred primarily by volume diffusion with a possibility that surface diffusion plays an important role in the early phase. Subsequent work by others, notably Kingery and Berg(13) who were the first to treat the grain boundary as a vacancy sink and to measure the approach of particle centers during sintering, has led to the same conclusions. They are also valid for the sintering of oxide ceramics, however, in materials such as sodium chloride that have a high vapor pressure, the evaporation-condensation mechanism controls neck growth.

The results of the various investigators who have worked on the problem and obtained different
TABLE I

Exponents in Kuczynski's Neck Growth Equation

<table>
<thead>
<tr>
<th>Sintering Mechanism</th>
<th>m</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscous flow</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Bulk diffusion</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>Surface diffusion</td>
<td>7</td>
<td>3</td>
</tr>
<tr>
<td>Evaporation and condensation</td>
<td>3</td>
<td>1</td>
</tr>
</tbody>
</table>

values for L(t), m, and n are summarized in the review article by Thummel and Thomma. When expressed in terms of linear shrinkage of the powder compact, all the results can be put in the form

\[
\frac{\Delta L}{L} = \left( \frac{KD v_{SA}}{kTn} \right)^m
\]

(22)

where D is the atomic diffusion coefficient and K is a constant whose magnitude depends on the geometry. The values of m range between 0.4 and 0.5 and that of n is usually 3.

The object of much of this work was to obtain more precise relations by employing somewhat less restrictive assumptions than those used by Kuczynski. By examining data according to these relations it was hoped that more clear-cut conclusions about mechanism would be possible and, in the case of diffusion controlled sintering, an accurate value for the magnitude of the diffusion coefficient of the controlling species could be obtained. "Accurate" in this case means a value near that measured independently for the volume self-diffusion of the slowest diffusing atomic species in the solid. The conclusions of all the later work have not essentially changed the basic form of Kuczynski's results nor his conclusions.

With regard to diffusion coefficients, none of the neck growth equations can be relied upon to yield values having anywhere near the reliability of those obtained from tracer measurements. Thus in the case of a material like Cr₂O₃, where the oxygen diffusion is many orders of magnitude slower than that of the chromium, the diffusion coefficient obtained from sintering experiments is nearer that of oxygen than chromium. In the case of Al₂O₃, however, where the tracer measured self-diffusion of oxygen and aluminum in polycrystalline samples are only about an order of magnitude different, the sintering values do not clearly distinguish the species that controls the sintering rate.

The work so far referred to has not been concerned with the influence of grain boundary diffusion. Kuczynski and many others have felt that the grain boundary is such a restricted channel that it cannot transport matter at a rate comparable to that of the other mechanisms in spite of the high diffusion coefficient in it. They have made approximate theoretical calculations to support this position. Johnson and Cutler, on the other hand, have contended that grain boundary diffusion is a significant contributor to neck growth in the initial stage. They have analyzed the initial shrinkage of Al₂O₃ and concluded that it is controlled by grain boundary diffusion. More recently, Johnson has published a paper describing a model on the basis of which volume, grain boundary, and surface diffusion coefficients may be obtained from measurements of neck growth and compact shrinkage during initial stage sintering.

7.6 Intermediate Stage Sintering Models

The initial development of a theory of intermediate stage sintering has been due largely to the work of Coble and his collaborators. The essential features of their approach were developed in Coble's first paper. In this he assumed all grains to have the same unchanging size and shape. The shape was that of a tetrakaidecahedron, a space-filling polyhedron, all of whose edges have the same length. The pores were likewise assumed to be of the same size, having the shape of circular cylinders, and lying along all grain edges. Using a greatly simplified model to describe the vacancy flow by volume diffusion from a single pore to the boundaries of the adjacent grains, he obtained the following equation for the densification

\[
P = P_0 - \frac{KD}{GkT} v_{SA} (t-t_0).
\]

(23)

where P is the porosity; t is time; D is the diffusion coefficient of the sintering-rate limiting species; G is the grain size which is related to the edge length of the polyhedron; K is a geometrical factor; and the subscript 0 indicates an initial value. Coble has used this equation to obtain values for the diffusion of Cu in Cu and Al in Al₂O₃ that are close to those obtained by tracers. In general, however, the values of D obtained using Eq. (23) are larger than those measured with tracers.

Aside from the fact that most intermediate stage sintering data are better fitted with a straight line if the porosity is plotted against the logarithm of the time rather than the time as indicated in Eq. (23), the derivation of that equation is most vulnerable to criticism on the basis that it does not include grain growth. Grain sizes may change by as much as an order of magnitude or more during this stage, which causes a reduction of the number of pores and a tendency to increase their average size as a consequence of coalescence.

Johnson has proposed a technique whereby grain growth may be taken into account. His method does not yield an explicit relation between porosity
and time. Rather it is a procedure by which the measured shrinkage rate at various times may be combined with stereographic measurements made on polished sections of samples, whose sintering was interrupted at those times, to yield values for the grain boundary and volume diffusion coefficients. It has never been applied, probably because of the difficulties inherent in preparing polished sections of porous compacts that can show up the internal structure to the degree of fidelity required.

More recently, Rosolowski and Greskovich(20) have analyzed intermediate stage sintering in a very general way. They assumed that pores were cylindrical and located on grain edges but they allowed a distribution of radii to occur, and not all edges had to contain pores. Similarly, no restriction was placed on the sizes and shapes of the grains, and grain growth according to any time dependence was allowed to occur. They assumed that pore shrinkage occurred by volume diffusion since their analysis showed this to be the dominant mechanism for the range of pore sizes usually observed in the intermediate stage. The equation obtained was

$$\ln(1-P) = \frac{K_D v}{kT} \int_{t_0}^{t} \frac{dt}{G^3_{\text{avg}}} + \ln(1-P_0). \quad (24)$$

where $K$ is a geometrical factor and the factor in the denominator of the integrand is the cube of the average grain diameter. For the usual case when the cube of the average grain diameter is linearly proportional to time, this equation predicts that porosity will be approximately proportional to the logarithm of time (as has been observed) since the leading term in the expansion of $\ln(1-P)$ is just $-P$.

The equation was applied to the analysis of the sintering of Cu, Al₂O₃, and BeO where simultaneous porosity and grain size determinations have been made experimentally. The data were in each case very well fitted to a straight line when plotted as $\ln(1-P)$ versus the integral. The values obtained for the activation energy of diffusion were also close to the tracer values. This was expected since the vacancy diffusion model used was expected to overestimate the vacancy flow for a pore but it could not, a priori, be decided by how much.

7.7 Final Stage Sintering Models

The final stage of sintering has been studied very little. The primary reason for this apparent lack of interest is probably the fact that the porosity is only a few percent and changing slowly. Thus the shrinkage in the very late stages could only be studied by examining changes in the number of pores and their size distribution with time. This is well nigh impossible to do in the usual, opaque sample.

Coble(17) has analyzed the vacancy flow from a pore on a grain corner, and concluded that the porosity of a piece containing such pores should decrease linearly with time as a result of volume diffusion. The fact that the rate of porosity decrease is always much less than that predicted by the Coble equation has been explained by stating that the rate of flow of vacancies from a pore to a boundary decreases rapidly with increasing distance between the pore and the boundary. Since exaggerated grain growth in the final stage causes a large fraction of the pores to end up inside the grains, the shrinkage rate will thereby be greatly reduced.

Rosolowski and Greskovich(21) have examined the flow of vacancies by volume diffusion from pores in the final stage. They expressed their results in terms of the total vacancy flow from a small pore at the center of a large grain. They found that the vacancy flow from a pore increased slowly with decreasing distance from the grain boundary, being only about a factor of 3.5 greater when it was within 0.01 of its radius from the grain boundary than when it was at the center of the grain. When the pore was actually on the boundary, the factor was about 8. They also made measurements of the pore densities and size distributions by direct observation in the transparent polycrystalline ceramic Yttralox® and found that the pore size distribution remained almost unchanged between 33 and 180 hours of sintering, while the pore density decreased by a factor of 25.

This anomaly could be explained if it were assumed that all the small pores swept up by the boundaries of growing grains disappeared rapidly. However, if vacancy flow were by volume diffusion, their theoretical results predicted that a considerable reduction in the size of the pores left inside the grains should have occurred in the same time. Since that was not the case, they concluded that grain boundary diffusion must be operating to rapidly shrink small pores on grain boundaries in the final stage.

8. SUMMARY

The term "sintering" is applied to those phenomena which occur when a metal or ceramic powder is transformed into a dense, solid product. Fundamental investigations of the process have demonstrated that, in most cases, the primary motivation for sintering is the tendency to reduce the surface energy of the system by joining particles and eliminating pores, and that a most important mechanism of accomplishing this is matter transport by solid-state diffusion.

It would be of considerable interest and importance if, through a fundamental understanding of the sintering process, it were possible to predict the influence of the major processing variables upon the rate of sintering and the properties of the product. There are, however, many factors such as particle size and degree of aggregation in the unsintered compact, the furnace atmosphere, grain growth during
sintering, etc., that influence the course of the process. As a result, the theoretical prediction of specific values of processing parameters, such as the sintering time and temperature required to produce a given product, is substantially impossible. On the other hand, the existing understanding is sufficient to most elegantly assist in the empirical development of procedures for producing a desired product from a powder.

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REFERENCES


