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## A Phenomenological Theory of Sintering

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**ABSTRACT.** Sintering occurs when powders are heated to temperatures near their melting points. This paper deals with the rapid increase of density during the sintering of single substances. The increase of density cannot be explained by volume diffusion of vacant lattice sites or surface migration of atoms, but must involve macroscopic flow. The driving force for this flow is surface tension, and an equation connecting the rate of shear strain with the shear stress defines the resistance to deformation.

The density of a compact is calculated as a function of the time for two different laws of deformation, (a) that for a solid with a Newtonian viscosity, and (b) that for a Bingham solid which has a yield point and a rate of shear strain proportional to the difference between the applied shear stress and a yield stress. The effect of gas in the pores is calculated in the case of the viscous law.

The theory assumes that the pores are equal spheres and predicts that densification is uniform throughout a compact, independently of its shape and size, and suggests that gas pressures of a few atmospheres applied to the outside of a compact may appreciably increase the rate of sintering.

Relevant experiments and previous theories are examined critically, and it is shown that while the viscous model may explain the sintering of glasses it cannot explain that of metals. However, the experimental data can be explained by a model showing a yield point: on such a model the interaction of one pore with its neighbours is vital, so that pores in powder compacts close and isolated pores do not.

### § 1. INTRODUCTION

WHEN powders of metals, ionic crystals, or glasses are heated to temperatures near to their melting points, the powder particles weld together and the density of the compact changes: this process is known as sintering. Sintering has been used from the earliest times for fabricating solid lumps of metals, such as iron or platinum, which could not be melted; today it is still used to fabricate materials of high melting point such as tungsten and alumina. Since about the middle of the last century it has been possible to melt most metals, and although interest in sintering then waned, it has recently increased again because it is sometimes cheaper to press and sinter small awkwardly shaped parts than to cast and machine them. In addition, sintering techniques can be used to produce special products such as porous bearings and, by the inclusion of gas-producing materials in the compacts, expanded glass products. The history of sintering has been reviewed by C. S. Smith (1942).

Sintering is a process which reduces the surface area of the powder particles, and the driving force arises from the excess free energy of the surface of the powder over that of the solid material. The fundamental problem of sintering is to explain by what mechanisms this reduction of energy occurs. In this paper a phenomenological theory of the sintering of single substances is developed; the atomic mechanisms operating remain obscure, but attention is drawn to certain basic phenomena which must be explained, and to the necessity for further experimental work. The literature dealing with the sintering of metals has been reviewed by Rhines (1946) and by Shaler (1949).

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At least two processes occur during sintering: (*a*) the powder particles weld together and the pores between them become more nearly spherical, and (*b*) the density of the compact increases. Although these two changes proceed simultaneously and the driving force for both arises from the excess surface free energy of the powder over that of the bulk material, they may occur by different mechanisms. The main theme of this paper is to explain the remarkably rapid increase of density which occurs during sintering. In §2 it is shown that the observed increase of density cannot be due to the volume diffusion of vacant lattice sites or surface migration of atoms, and that probably both volume diffusion and non-uniform flow are responsible for the sphering of the pores. In §3 it is shown that the driving force for sintering is surface tension, and that at high temperatures it is permissible to assume an equation of mechanical state connecting the rate of shear strain of the material with the shear stress at constant temperature.

So that the reader may follow the general trend of the arguments to their final conclusion, the mathematical calculation of the density of a compact as a function of the time is deferred until §5. The calculation is carried out for two different equations of state: (*a*) that for a solid with a Newtonian viscosity, for which the rate of shear strain is proportional to the shear stress, and (*b*) that for a Bingham solid which has a yield point and a rate of shear strain proportional to the difference between the applied shear stress and the critical shear stress. The effect of gas in the pores is considered in §6, and some limitations on the possible atomic mechanisms in §7. In §8 some suggestions are made for experimental work.

Shaler and others have made certain experiments which were designed to test Frenkel's theory that sintering is due to viscous flow induced by surface tension. In §4 both the theory and the experiments are examined critically, and it is shown that although the viscous hypothesis may explain the sintering of glasses it cannot explain the sintering of metals. It is indicated in general terms how all the experimental results can be explained if it is supposed that the material shows a yield point. Attention is drawn to the lack of experimental data concerning the mechanical properties of metals at sintering temperatures.

In discussing the work of other authors, the present authors have sometimes drawn different conclusions from the original authors, or stated conclusions which did not appear in the original paper. Therefore many matters have been discussed at greater length than might otherwise have been the case.

## §2. SPHERING OF THE PORES

Before proceeding with the main theme it is convenient to show that neither volume diffusion of vacant lattice sites nor surface diffusion of atoms can account for the observed changes in density, and to discuss the experiments relating to the sphering of the pores.

All the lattice points of a crystal in thermal equilibrium at a finite temperature are not occupied by atoms. At the melting point of copper the concentration of vacant lattice sites is about 1,000 times the concentration of atoms in the vapour phase. These vacant lattice sites can move through the lattice and are responsible for self-diffusion. Just as the equilibrium vapour pressure is greater outside a convex surface\* than outside a concave surface, so the equilibrium concentration of vacant lattice sites is greater inside a concave surface than inside a convex surface.

\* A surface is described as concave or convex according to its appearance to an observer situated in the vapour phase.

Now volume diffusion alone can only change the density of a compact provided that vacant lattice sites diffuse from the interior to the outer boundary. This is a negligibly slow process: for, in order that pores in the centre of the compact should disappear, it is necessary that diffusion should occur over large distances. A simple calculation shows that if the excess concentration of vacant lattice sites in copper at  $1,000^{\circ}\text{C}$ . is produced by pores of  $1\mu$  radius, and diffusion has to take place over a path of 1 mm., then the decrease of linear dimensions due to volume diffusion will be only  $3 \times 10^{-6}\text{ cm/day}$ ; Kuczynski's experiments (1949) indicate that at  $1,000^{\circ}\text{C}$ . surface diffusion is even less effective in transporting material. Further, if volume diffusion were responsible for the increase of density, no net diffusion to the surface could take place until there were no pores between the surface and the point under consideration. Sintering would then occur from the surface inwards, and the time of sintering would be a function of the shape and size of the compact. This conclusion is the opposite of that drawn in § 5 (i) from the theory developed later in this paper.

On the other hand, although diffusion cannot change the density of a compact appreciably, it can move matter over short distances and so change the shape of the pores. Diffusion moves atoms from the high-energy convex parts of the surface to the lower-energy concave parts so that the pores become more spherical and their surface area less. The following phenomena may be explained in terms of a mechanism of this type. Chalmers, King and Shuttleworth (1948) observed that scratches on a silver surface filled up when it was heated in air near to its melting point: they suggested that the most important mechanism for transfer of atoms was surface diffusion. Kuczynski (1949) placed a number of copper and silver spheres ( $\sim 100\mu$  diameter) on a plane surface of the same metal and heated them in an inert atmosphere near to their melting points. The crack between the sphere and the plane gradually filled up, and this was attributed to volume diffusion of vacant lattice sites.

Kuczynski derives a relation between the rate of filling up of the cracks and the self-diffusion coefficient of the metal. He shows that, for copper and silver, the self-diffusion coefficient derived from his experiments has the same activation energy as that derived from experiments with radioactive tracers, and has roughly the same magnitude. Kuczynski also claims to be able to distinguish between the mechanisms of volume and surface diffusion by a difference in the dependence of the size of the neck on the time. This is probably not correct as Kuczynski's theoretical treatment of the problem is over-simplified. A new treatment by Cabrera shows that the dependence of the size of the neck on the time is the same for both mechanisms, and that surface diffusion can only be distinguished from volume diffusion by its lower activation energy.\* Thus, because of the numerical agreement between the activation energies, the present authors conclude that, in Kuczynski's experiments, the dominant mechanism for transporting matter over short distances at sintering temperatures is volume diffusion. Chalmers, King and Shuttleworth's observation is presumably due to volume diffusion also.

However, it is shown later in this paper that plastic flow and the interaction of one pore with its neighbours are vital to the rapid increase of density during sintering. These two factors were missing in Kuczynski's experiments, so that volume diffusion will not necessarily be the only mechanism causing sphering of the pores during sintering. In fact, differential flow can also lead to sphering,

\* The authors are greatly indebted to Dr. Cabrera for privately communicating these results.

and may possibly be the dominant mechanism for sphering, particularly in the final stages. For, anticipating later sections, the inward pressure due to surface tension will be greatest in the neighbourhood of those parts of a pore which have the greatest concavity, and so the greatest flow would be expected in these parts. When a sphere stands on a plane, the shear stress will be almost zero everywhere except in the neighbourhood of the neck. Thus, although the critical shear stress is probably exceeded in the neck and the material there plastic, the bulk of the sphere (and the plane below) will not be able to flow plastically, and the constraint thus imposed will effectively prevent flow occurring.

### §3. THE DRIVING FORCE AND RESISTANCE TO DEFORMATION

#### (i) *The Driving Force is Surface Tension*

Shaler and Wulff (1948) showed experimentally that forces as small as those of surface tension may cause sintering. The surface tension acting in the surface of a pore of radius  $30\mu$  in a copper compact is equivalent to a negative (inward) pressure of about one atmosphere inside the pore. Shaler superposed upon the surface forces a gas pressure of one atmosphere and measured the change of density of a compact. An unpressed copper compact was heated in an inert gas until the pores sealed and an equilibrium relative density equal to 82% of the density of solid copper was obtained; in this state, because of the surface tension, the gas pressure inside the pores was greater than that outside. The gas pressure outside the compact was then removed and, under the driving force of one atmosphere pressure, the density decreased to a new equilibrium relative density of 60% in less than eight hours.

Some authors have suggested other forces. In commercial practice metal powders are pressed at 20–30 tons/in<sup>2</sup> before sintering, and this will cold-work the powder. It has been suggested that the strain energy of cold-work is the driving force for sintering. This is not very likely since, at high temperatures, recovery and recrystallization occur in a few seconds, and any strain energy will be dissipated before it can be used to aid sintering. It should be noted that Shaler's experiment above was carried out with an unpressed powder.

#### (ii) *The Existence of an Equation of State*

In a compact formed from spherical particles in contact, an increase of density will occur only if the centres of the particles get closer. This can occur either by a substantially radial flow of material into the pores, or by transfer of material away from the areas of contact. Kuczynski's (1949) photo-micrographs seem to indicate that, after a sphere has been heated in contact with a plane for a number of hours, material is transferred from the plane towards the area of contact; the sphere is left standing on a pedestal. From this, and the fact that diffusion is incapable of explaining large increases in density, it is concluded that flow of the material on a macroscopic scale is required to explain increases in density.

During sintering, the temperatures are high and deformation occurs slowly compared with the rates of recrystallization and recovery. The material will anneal as deformation proceeds, its mechanical state will be the same at all times, and no strain hardening will occur. In these circumstances the rate of strain will depend only upon the stress and not upon the strain or the previous history of

the material. The equation which connects the rate of strain with the stress at constant temperature is an equation of mechanical state which defines the resistance to deformation.

While the energy released by recrystallization and recovery is irrelevant for determining the driving force, the rate at which these, or other annealing processes, occur will be factors which determine the rate of strain corresponding to a given stress, i.e. the equation of mechanical state.

The theory of sintering will be developed on the assumption that deformation is due to surface tension and that the material of the particles has homogeneous mechanical properties defined by an equation of state. It will be assumed that purely hydrostatic stresses and strains are unimportant in producing large deformations by flow; thus, the equation of state will be assumed to connect the rate of shear strain with the shear stress; for simplicity in the calculations, the material will also be assumed to be incompressible. The actual form of the equation of state is a matter for future experiments: glass is known to have a Newtonian viscosity, the rate of shear strain being proportional to the shear stress, while it is deduced from sintering experiments that crystalline metals should show a yield-point phenomenon which must be taken into account.

Both W. D. Jones (1937) and Bangham (1947) have previously recognized that sintering probably involved plastic flow.

#### § 4. THE KINETICS OF SINTERING

##### (i) *Experimental Data*

When metals are sintered large increases of density can occur in very short times. A compact of tungsten powder heated to just below its melting point has all its linear dimensions decreased by 17% in 15 minutes (Smithells 1945). Shaler (1949) finds that the relative density of an unpressed powder of copper increases from 50% to 95% after heating for six hours at 930°C., a decrease in linear dimensions of 24%. The melting point of copper is 1,083°C.

Shaler and his collaborators (Shaler and Wulff 1948, Shaler 1949, Udin, Shaler and Wulff 1949) have attempted to develop a theory of sintering based upon Frenkel's ideas (1945) concerning the viscosity of solids. They have performed three important experiments in which they try to show that copper has a Newtonian viscosity at high temperatures.

In the first set of experiments unpressed compacts of spherical copper particles, all of about 110  $\mu$  radius, were heated in a vacuum for various periods up to 45 minutes; the density increased by amounts up to 30%.

In the second set Shaler bored cylindrical pores of radius 170  $\mu$  along the axis of a wire of radius 1,650  $\mu$  and measured the decrease of pore radius after heating to 1,000°C. for 48 hours. The results were erratic, and of three specimens measured the radius of one pore decreased monotonically by 8%, while the radii of the other two pores increased by 5% during the first 24 hours and then decreased to their original value during the second 24 hours.

In the third set of experiments Udin *et al.* suspended a series of weights by means of fine copper wires (radius 36  $\mu$  and 64  $\mu$ ) which were then heated to temperatures between 950°C. and 1,050°C. They found that if there were no weights on a wire it shrank because of the surface tension acting upwards, but if the weight overbalanced the surface tension the wire stretched. They measured the final strain of wires heated for between one and five days, but their technique did not

enable them to measure the extension of one wire as a function of time. At 1,050°C. surface tension acting alone caused the wire to contract 0.4% in one day.

By finding the weight necessary to balance the surface tension Udin was able to calculate the surface tension of solid copper. He gives a value  $1.4 \times 10^8$  dyne/cm. This value agrees roughly with the theoretical value of the surface free energy per unit area derived by Huang and Wyllie (1949), viz. 1,820 erg/cm<sup>2</sup>.

### (ii) Previous Theories of Sintering

Frenkel (1945) supposed that the increase of density during sintering occurs because both amorphous and crystalline materials behave at high temperatures as though they were liquids with Newtonian viscosities; the driving force was supposed to be due to surface tension. He suggested that this viscosity arose because of the existence of vacant lattice sites in thermodynamic equilibrium, and predicted a value of the coefficient of viscosity  $\eta = kT/D\delta^3$ , where  $T$  is the absolute temperature,  $D$  is the coefficient of self-diffusion and  $\delta^3$  is the volume per atom. Using the data of Maier and Nelson (1942) for  $D$ , Frenkel's formula predicts that the viscosity of copper at 1,000°C. is  $3.1 \times 10^8$  poise\*. However, Nabarro (1948) showed that Frenkel's calculation of the coefficient of viscosity was not correct for crystalline materials, and that a crystal which contained no imperfections other than vacant lattice sites would not be viscous. On the other hand, if the crystal had a mosaic structure it would show a Newtonian viscosity, and the coefficient of viscosity would be greater than that given by Frenkel's formula by at least a factor  $l^2/\delta^2 \sim 10^8$ , where  $l$  is the distance between mosaic boundaries.

Shaler and his collaborators have followed Frenkel's ideas and performed experiments which throw some light on the flow of metals at very high temperatures. Shaler concluded from his experiments that copper has a Newtonian viscosity small enough to explain sintering: the present authors conclude from the same experiments that the sintering of copper cannot be explained in terms of viscous flow.

#### The Apparent Viscosity of Copper at 850°C. (in poise)

Shaler and Wulff from sintering†	$2.2 \times 10^9$
Udin <i>et al.</i> from creep‡	$7.8 \times 10^{13}$
Nabarro's theory of vacant lattice site diffusion	$3.4 \times 10^{12}$

The argument may be put qualitatively in the following way. If copper behaves as a viscous liquid with surface tension, then, provided their radii are equal, the rate at which a pore in a porous mass closes should not be expected to differ by more than a factor 10 from the rate at which an isolated pore closes, or the rate at which an unloaded wire contracts. But the experiments show that the radii of pores in a powder compact decrease by 20% in 45 minutes at 850°C., while the radii of isolated pores showed no systematic decrease after heating for

\* According to Kaye and Laby (1944) the viscosity of Lyle's golden syrup is  $1.4 \times 10^8$  poise at 12°C.

† The value given is derived from data read from Shaler and Wulff's curves and is calculated by using the theory of § 5 (iii). Shaler and Wulff derive a value  $5 \times 10^8$  sec/cm<sup>3</sup>; the dimensions of the poise are gm/cm<sup>2</sup>sec.

‡ Udin uses a formula due to Frenkel which is in error by a factor 2. His results should be expressed in the form  $\eta = 260 \exp 59,000/RT$ .

48 hours at 1,000° c., and the length of a free wire only decreased by 0.4% per day at 1,050° c.

The argument can also be expressed quantitatively by estimating the apparent viscosities for the various experiments. This is done in the Table, where the values are compared with the order of magnitude expected on Nabarro's theory; no estimate can be made in the case of the single-pore experiments, but the results are not inconsistent with those derived from Udin's wire-pulling experiment. The sintering experiment gives a value  $10^4$  times smaller than the wire-pulling experiment, and it is evident that the flow observed by Udin does not contribute appreciably to sintering; it probably arises from the Nabarro mechanism.

### (iii) *The Mechanical Properties of Copper at High Temperatures*

No experiments have been made with the primary object of determining the deformation of metal specimens as a function of time and stress at sintering temperatures. It is therefore necessary to deduce the mechanical properties at these temperatures from more or less indirect evidence.

We have already seen that at the low stresses used in the wire-pulling experiments copper probably has a Newtonian viscosity. On the other hand, the sintering experiments cannot be so explained; for these the effective stress is somewhat higher.

It appears that no other experiments have been made on the mechanical properties of metals at high temperatures. However, Chalmers (1936) has measured the mechanical properties of tin at room temperature (212° c. below the melting point). He finds that for low stresses viscous flow occurs, the viscosity being  $10^{15}$  poise, but that when the maximum shear stress exceeded a critical value of  $10^7$  dynes/cm<sup>2</sup> a vastly increased rate of deformation occurred, viz. a linear rate of strain of 15% per day at a shear stress of  $1.4 \times 10^7$  dynes/cm<sup>2</sup>.

The authors suggest that the mechanical properties of copper at high temperatures are similar to those found for tin, and that the important mechanism for deformation during sintering occurs when the yield stress is exceeded; Udin did not observe the yield stress because his stresses were too low. It will be shown that this view can explain the three experiments described in § 4 (i), and in § 5 (vi) it will be shown that the critical shear stress for copper at 850° c. should be at least  $2.5 \times 10^5$  dynes/cm<sup>2</sup> or possibly greater by a factor less than 5. At room temperature the critical shear stress is  $10^7$  dynes/cm<sup>2</sup>.

It is convenient at this point to formulate mathematically the two equations of mechanical state which will be used in the subsequent mathematical treatment. For a Newtonian viscous solid such as a glass the rate of shear strain  $\dot{s}$  is proportional to the shear stress  $\tau$ :

$$\tau = \eta \dot{s}, \quad \dots\dots (1)$$

where  $\eta$  is the coefficient of viscosity. This is represented in Figure 1 by the straight line through the origin. For a Bingham solid (Burgers 1939), which is appropriate to a crystalline metal,

$$\text{and } \left. \begin{array}{l} \tau = \eta \dot{s} + \tau_c, \quad |\tau| > |\tau_c|, \\ \dot{s} = 0, \quad |\tau| < |\tau_c|, \end{array} \right\} \dots\dots (2)$$

where  $\tau_c$  is the critical shear stress and changes sign so as always to have the same sign as  $\dot{s}$  (see Figure 1); for simplicity anisotropy of plastic properties will be

neglected. This relation between  $\tau$  and  $\dot{s}$  is the simplest which exhibits a yield point, and the instantaneous viscosity  $\eta = \tau/\dot{s}$  decreases as the speed of deformation increases.

(iv) *Interpretation of Experiments on the Bingham Solid Model*

What really has to be explained is the qualitatively different behaviour of isolated pores and pores in the neighbourhood of other pores. In succeeding sections the problem is developed mathematically; here only a qualitative account is given of how this difference is explained by the hypothesis that a yield point exists.

In the neighbourhood of an isolated pore the shear stress caused by surface tension decreases with distance from the centre of the pore. Thus beyond a

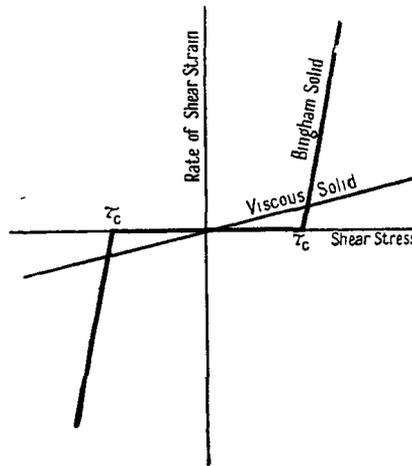


Figure 1. The relation between the rate of shear strain and the shear stress for a viscous solid and a Bingham solid.

certain distance the yield stress is not exceeded, and no flow can occur because the material beyond cannot flow. On the other hand, in a porous compact the plastic regions surrounding each pore will overlap, and flow will occur because the yield stress is exceeded everywhere; the interaction between pores is vital.

#### § 5. THE THEORY OF SINTERING

In accordance with the discussion given in § 3, it will be assumed that deformation during sintering is due to surface tension and that the material of the particles has homogeneous mechanical properties defined by an equation of state connecting the rate of (octahedral) shear strain with the (octahedral) shear stress. The material will also be assumed to be incompressible. Further, in order to arrive at definite quantitative results and to simplify the calculations, it has been convenient to consider a special model in which all the pores are isolated equal spheres distributed at random in the real solid material. This assumption is considered at the end of sub-section (1) and does not essentially change the character of the results.

In the next sub-section results independent of the form of the equation of state are deduced and the general nature of the flow during sintering is indicated;

the model used for making detailed calculations is described and the general equation of energy for the flow is set up. Two equations of state, that for a viscous solid and that for a Bingham solid, are considered in detail in sub-sections (iii) and (iv), and equations giving the density as a function of the time are derived. In sub-section (v) the effect of an initial viscosity is considered. Finally, in sub-section (vi) the results are compared with the experiments described in § 4 (i) and an estimate made of the critical shear stress for copper.

(1) *Conclusions Independent of the Form of the Equation of State*

Consider a compact in which all the pores are spherical and of equal radius  $r_1$ . The surface tension  $\gamma$  acting in the surfaces of the pores is equivalent to a pressure  $-2\gamma/r_1$  inside all the pores; this produces shear stresses in the material and the pores close. Now because the material is supposed incompressible, the application of an additional hydrostatic pressure to the inside of all the pores and to the external surfaces of the compact will cause no strain and hence no change in the rate of strain. If this additional pressure is  $+2\gamma/r_1$ , the resultant pressure will be zero inside all the pores and  $+2\gamma/r_1$  on the external surfaces. Thus the effect of surface tension in closing the pores is equivalent to the application of an external pressure to the surface of the compact. Incompressibility is not essential to this result, it is sufficient that the rate of strain be independent of the hydrostatic pressure.

If attention is directed not to the detailed nature of the flow in the immediate vicinity of a pore but to the behaviour of volume elements that contain a large number of pores, then the compact can be regarded as forming a homogeneous continuum. When a hydrostatic pressure is applied to the surface of the continuum, its volume slowly decreases; the volume of the real material remains unchanged, but because of shear stresses its shape changes and it flows into the pores. Now the application of a hydrostatic pressure to the surface of a homogeneous continuum produces an equal uniform hydrostatic pressure at all points throughout the whole volume, independently of its shape or size (Love 1944). Thus the rate of increase in density of any element of volume will be uniform throughout the whole body and the rate of sintering will be independent of the shape or size of the compact (cf. § 2). A consequence of this uniform contraction is that to an observer situated on a pore, and moving with it, all distant pores will appear to approach with a velocity proportional to their distance (see Eddington 1933). During this flow the size of the pores will decrease, their centres will approach each other, but the total number of pores will remain unchanged.

Even when the pores are not equal in size and are not spherical the rate of increase in density will be uniform throughout the whole compact, provided the distribution of pore shape and size is the same in all parts of the compact. For if a mean pressure  $2\gamma/\bar{r}_1$  is applied to all surfaces of the real material, where  $\bar{r}_1$  is some mean radius of curvature of all the pore surfaces, then the resultant forces on the real material are a pressure  $2\gamma/\bar{r}_1$  over the external surface of the compact and a distribution of pressure over the surfaces of the pores the effect of which is zero on the average. This problem is discussed in more detail by Mackenzie (1950). When the pores are not spherical flow will contribute to their sphering. When the pores are not equal in size the small pores will shrink and disappear more rapidly than do the larger pores, so that the total number of pores will decrease with time of sintering.

(ii) *The Model*

The problem is to deduce the properties of the equivalent homogeneous material from the properties of the real material and the number and the size of the pores. A convenient self-consistent method of approximation has been indicated by Frohlich and Sack (1946); their method is equivalent to a perturbation calculation and is valid when the volume of the pores is sufficiently small compared with the volume of the material. This method is used in the following calculations.

Every pore of radius  $r_1$  will be surrounded by a spherical shell of the real incompressible material, out to some radius  $r_2$  which will be chosen later (Figure 2). When an external pressure is applied there will be certain stresses

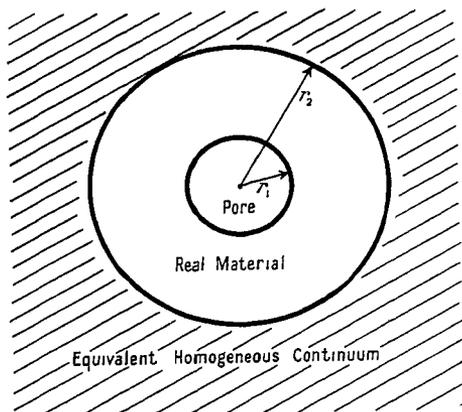


Figure 2. The model. The reaction of material outside the sphere of radius  $r_2$  is calculated by replacing it by an equivalent homogeneous continuum.

acting across the outer boundary of this shell; these stresses represent the combined effect of the external pressure and the interaction of the rest of the porous medium. If these stresses were known, the flow of the material inside the shell could be calculated and the decrease in volume determined; then by summation for all pores the total decrease in volume is known since the real material is incompressible. The approximation consists in replacing the material outside the spherical shell (including the pores it contains) by an equivalent continuum. For this approximation to be consistent it is necessary that both the macroscopic flow and the density of the equivalent continuum should not be altered by the presence of the pore and its surrounding shell.

Now the stress in the continuum is everywhere a hydrostatic pressure equal to the applied pressure. Thus the first condition of consistency implies that the stress at the outer surface of the spherical shell containing the pore is a pressure equal to the applied pressure, or the rate of increase of density of the continuum is the same as that of the pore and its surrounding shell when the same pressure is applied to its outer surface. The second condition of consistency determines  $r_2$ ; if  $\rho$  is the density of the compact relative to that of the real material, then the condition that the pore and its shell have the same density as the compact is

$$\rho = 1 - (r_1/r_2)^3. \quad \dots\dots(3)$$

The approximations of this treatment are valid when  $r_1/r_2$  is small compared with unity, and it is not clear how accurate the treatment will be when the pores are close together. However, the results are correct as  $\rho$  tends to zero, so that the method should give the correct order of magnitude for all densities (Mackenzie 1950).

The problem has now been reduced to the calculation of the rate of decrease in radius  $r_1$  of a spherical pore, surrounded by a shell of incompressible but shearable material, when a pressure  $-2\gamma/r_1$  is applied inside the pore. In the case of an isolated pore the outer radius  $r_2$  would be infinite; the finite value for  $r_2$  takes into account the interaction between the pores. The rate of closing will be calculated by equating the energy dissipated by the flow of the material in the shell to the work done by surface tension; the kinetic energy of the material will be negligibly small, so that it is possible to treat the problem as one of a steady state.

Consider a regular octahedron in which the line joining a pair of opposite vertices is directed along a radius of a pore. Then when a hydrostatic pressure is applied inside the pore the flow of material is radial and the faces of the octahedron are subject only to shear strain—the octahedral shear strain. For a Bingham solid the instantaneous viscosity  $\eta$  is a function of the shear strain. Since the latter is a tensor quantity, some combination of the components must be chosen on which  $\eta$  is to depend. By analogy with the theory of plasticity (Nádai 1937), it will be assumed that at constant temperature the equation of state connects the rate of octahedral shear strain with the corresponding octahedral shear stress.

If the rate of radial strain is  $\dot{\epsilon}$ , the condition of incompressibility shows that the rate of strain in any direction perpendicular to the radius is  $-\frac{1}{2}\dot{\epsilon}$ ; these are three principal directions of stress and strain. The corresponding octahedral shear strain is

$$\dot{s} = \sqrt{2} \dot{\epsilon}. \quad \dots\dots(4)$$

The rate of dissipation of energy in any element can be found from the theory of viscosity as given, for example, by Lamb (1932). In Lamb's notation  $a = \dot{\epsilon}$ ,  $b = c = -\frac{1}{2}\dot{\epsilon}$ ,  $f = g = h = 0$ , and the rate of dissipation of energy per unit volume \* is

$$\dot{E} = 3 \dot{\epsilon}^2 \eta. \quad \dots\dots(5)$$

The viscosity may be a function of position. The corresponding results for a cylindrical pore are  $\dot{s} = 2\dot{\epsilon}$  and  $\dot{E} = 4\dot{\epsilon}^2 \eta$ . The relations have been obtained by Eshelby (1949) by elementary means.

If  $u_1$  is the radial velocity of the surface of the pore, surface tension does work at a rate  $-4\pi r_1^2 u_1 2\gamma/r_1$ , and on equating this to the energy dissipated throughout the whole volume of the shell

$$-2\gamma r_1 u_1 = 3 \int_{r_1}^{r_2} r^2 \dot{\epsilon}^2 \eta(\dot{\epsilon}) dr. \quad \dots\dots(6)$$

Now, since the real material is incompressible, the radial velocity at any radius is inversely proportional to the square of the radius. Thus  $u = u_1 r_1^2 / r^2$  and the rate of radial strain

$$\dot{\epsilon} = \frac{du}{dr} = -\frac{2u_1 r_1^2}{r^3}. \quad \dots\dots(7)$$

\* Frenkel (1945), treating the same problem, assumes wrongly that  $b = c = 0$ , so that his result is two-thirds of ours.

When  $\eta(\dot{\epsilon})$  is given explicitly, (6) and (7) can be solved for  $u_1$  and, by means of (3), a differential equation for  $\rho$  as a function of time derived. This is done in the following sub-sections for  $\eta = \text{constant}$  (viscous solid) and  $\eta = \eta_\infty + \tau_0/\dot{s}$  (Bingham solid).

(iii) *The Sintering of a Viscous Solid*

For a solid which has a Newtonian viscosity,  $\eta$  is independent of the rate of strain. On substituting (7) into (6) and making use of (3) it is found that

$$u_1 = -\frac{\gamma}{2\eta} \frac{1}{\rho}. \quad \dots\dots(8)$$

For an isolated pore  $\rho = 1$ , so the factor  $1/\rho$  represents the effect all the other pores have on the rate of closing of one pore; since  $\rho$  will always be greater than  $\frac{1}{2}$  in a powder compact, a pore in a compact will never close at more than double the rate of an isolated pore. Equation (8) is also appropriate to the closing of a cylindrical pore.

In experiments on sintering, the compact is usually held at constant temperature and the density measured as a function of time. The volume of real material in the compact does not change, nor does the total number of pores, if they are all equal. It is therefore convenient to obtain a relation between the relative density and the time of sintering in terms of  $n$ , the number of pores per unit volume of the real material, and  $\gamma$  and  $\eta$ . The volume of each pore is  $4\pi r_1^3/3$ , so that equation (3) gives

$$r_1 = \left(\frac{3}{4\pi}\right)^{\frac{1}{3}} \cdot \frac{(1-\rho)^{\frac{1}{3}}}{\rho^{\frac{1}{3}}} \cdot \frac{1}{n^{\frac{1}{3}}}, \quad \dots\dots(9)$$

and, since  $u_1 = dr_1/dt$ ,

$$\frac{d\rho}{dt} = \frac{3}{2} \left(\frac{4\pi}{3}\right)^{\frac{1}{3}} \frac{\gamma n^{\frac{1}{3}}}{\eta} \cdot (1-\rho)^{\frac{2}{3}} \rho^{\frac{4}{3}}.$$

When this is integrated the time is obtained as a function of  $\rho$ ,

$$\frac{\gamma n^{\frac{1}{3}}}{\eta} (t-t_0) = \frac{2}{3} \left(\frac{3}{4\pi}\right)^{\frac{1}{3}} \int_0^e \frac{d\rho}{(1-\rho)^{\frac{2}{3}} \rho^{\frac{4}{3}}}, \quad \dots\dots(10)$$

and  $\rho$  is then determined as a function of  $t$  by inversion. The indefinite integral is easily evaluated by means of the substitution  $x^3 = (1-\rho)/\rho$  and the result is

$$\frac{1}{2} \ln \frac{1+x^3}{(1+x)^3} - \sqrt{3} \tan^{-1} \frac{2x-1}{\sqrt{3}}.$$

In Figure 3 the curve  $a=0$  shows  $\rho$  as a function of the reduced time  $\gamma n^{\frac{1}{3}}(t-t_0)/\eta$ . The zero from which the time of sintering of any particular compact is measured is determined by the initial density, and in the Figure  $t=t_0$  is chosen, arbitrarily, to correspond to  $\rho=0$ . An increase in the number of pores per unit volume of material makes the abscissa scale correspond to a shorter time but does not change the curve. It is clear that sintering to unit relative density occurs in a finite time. If the reduced time corresponding to a given density is read off the curve and plotted as a function of  $(t-t_0)$  found experimentally, a straight line of slope  $\gamma n^{\frac{1}{3}}/\eta$  will be obtained;  $n$  can be estimated from the size and packing of the particles and so  $\gamma/\eta$  can be deduced.

Shuttleworth (1949a) has derived equation (10) by an alternative method involving the same assumptions. The problem of the steady flow of a viscous liquid is mathematically identical with the determination of the elastic displacement

in an incompressible solid, and so it is possible to solve the viscous problem by means of the known solution to the elastic problem. The problem is also discussed in more detail by Mackenzie (1950).

(iv) *The Sintering of a Bingham Solid*

The instantaneous viscosity of a Bingham solid is found from (2) and (4) to be

$$\eta = \eta_{\infty} + \tau_0 / \sqrt{2\dot{\epsilon}},$$

and if flow occurs at all,  $\tau_0$  and  $\dot{\epsilon}$  have the same sign. Substituting this value of  $\eta$  into (6) and using (7), it is found that

$$-u_1 = \frac{\gamma}{2\eta_{\infty}\rho} \left[ 1 - \frac{3\sqrt{2}\tau_0 r_1}{2\gamma} \ln \frac{r_2}{r_1} \right], \quad \dots\dots(11)$$

and  $\dot{\epsilon}$  or  $-u_1$  has the same sign as  $\tau_0$  only if

$$2\gamma/r_1 > 3\sqrt{2}\tau_0 \ln(r_2/r_1). \quad \dots\dots(12)$$

A pore will not close unless this condition is satisfied.

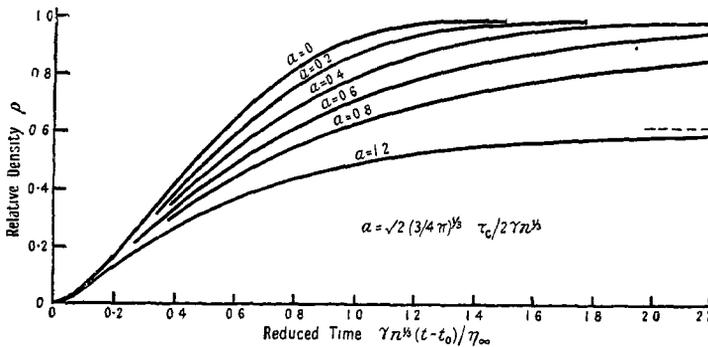


Figure 3. The relative density of a compact as a function of the reduced time when the real material of the compact behaves like a Bingham solid. The curve  $\alpha=0$  applies when the real material behaves like a viscous solid.

Equation (12) may be written in the form

$$2\gamma/r_1 > \sqrt{2}\tau_0 \ln \{1/(1-\rho)\}. \quad \dots\dots(12a)$$

Thus for a given initial density there is a critical size of pore such that a material containing smaller pores will increase in density while one containing larger pores will not.

A pore in a Bingham solid will behave quite differently according to whether it is near or far from other pores. An isolated pore will not close since  $r_2/r_1$  is large, whilst in a compact the interaction between the stress fields of the pores is vital and sintering will occur because of the small value of the ratio  $r_2/r_1$ . The corresponding criterion for closure of a cylindrical pore is

$$\gamma/r_1 > 2\tau_0 \ln(r_2/r_1). \quad \dots\dots(13)$$

This criterion is applicable to Shaler's experiments on isolated cylindrical pores because the pressure due to surface tension in the outer surface (including the ends) is small compared to pressure at the inner surface.

Using equations (3) and (9), the rate of increase of density of a compact is given by

$$\frac{d\rho}{dt} = \frac{3}{2} \left( \frac{4\pi}{3} \right)^{\frac{1}{3}} \cdot \frac{\gamma n^{\frac{1}{3}}}{\eta_{\infty}} \cdot (1-\rho)^{\frac{2}{3}} \rho^{\frac{1}{3}} [1 - a(1/\rho - 1)^{\frac{1}{3}} \ln \{1/(1-\rho)\}], \quad \dots\dots(14)$$

where

$$a = \sqrt{2} \left( \frac{3}{4\pi} \right)^{\frac{1}{3}} \cdot \frac{\tau_c}{2\gamma n^{\frac{1}{3}}}.$$

This equation was integrated numerically and, in Figure 3,  $\rho$  is plotted as a function of the reduced time  $\gamma n^{\frac{1}{3}}(t-t_0)/\eta_{\infty}$  for a number of values of the parameter  $a$ . The value  $a=0$  applies to a viscous liquid, and increasing values of  $a$  correspond to increasing values of the yield stress  $\tau_c$  or to decreasing values of  $n$ .

In Figure 4 the function

$$f(\rho) = (1/\rho - 1)^{\frac{1}{3}} \ln \{1/(1-\rho)\}$$

is plotted as a function of  $\rho$ . From equation (14) it is clear that sintering occurs only when  $af(\rho)$  is less than unity. When  $a$  is small this condition is satisfied for all  $\rho$  and sintering to unit relative density always occurs in a finite time. When

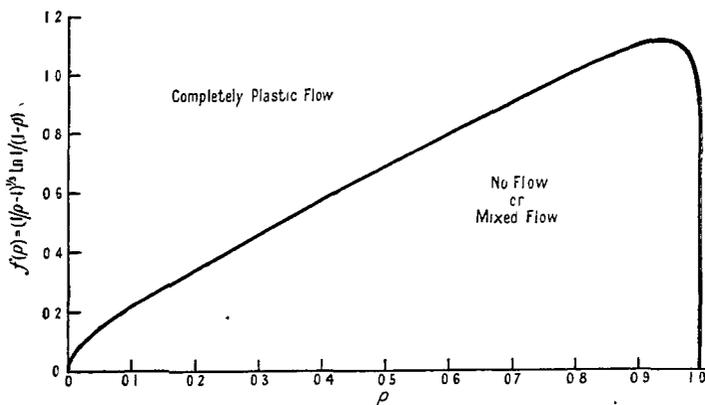


Figure 4. The function  $f(\rho)$  which determines the character of the flow in a compact.

$a$  is greater than 0.89 the rate of sintering decreases to zero as the density increases towards a value such that  $f(\rho) = 1/a$ ; if the initial relative density is less than 0.94 this limiting relative density is approached asymptotically. If, however, with the same value of  $a$ , the initial relative density is increased (e.g. by pressing), then at some value greater than 0.94 sintering will again begin and the compact will sinter to unit relative density in a finite time. This second branch of the curve begins at  $\rho = 0.998$  for  $a = 1.2$ , and is not shown in the Figure. The fact that  $f(\rho)$  tends rapidly to zero as  $\rho$  tends to unity indicates that very small pores will close even when they are at large distances apart.

#### (v) *The Effect of an Initial Viscosity*

It was assumed in the last sub-section that when the shear stress was less than  $\tau_c$  no movement occurred. This is not strictly true, and in this sub-section the effect of an initial viscosity is considered. It will now be supposed that for  $\tau < \tau_c$  the rate of shear strain is proportional to the shear stress, the constant of proportionality being  $1/\eta_0$ , corresponding to an initial coefficient of viscosity  $\eta_0$ ,

while for  $\tau > \tau_c$  the slope of the line defining the equation of state is assumed to be  $1/\eta_\infty$ , as for the Bingham solid just considered. The initial viscosity  $\eta_0$  will be at least ten thousand times larger than  $\eta_\infty$  for copper.

If the critical shear stress is nowhere exceeded, i.e.  $s_1 < \tau_c/\eta_0$ , the flow will be viscous everywhere and the equations of § 5 (iii) will apply; however, there will usually be a transition boundary inside which the material is flowing plastically, and outside which the material is flowing viscously. At this boundary (of radius  $r_0$ )  $\dot{s} = \tau_c/\eta_0$  and equations (4) and (7) give

$$\frac{r_1^3}{r_0^3} = \frac{-\tau_c r_1}{2\sqrt{2}u_1\eta_0}, \quad \dots\dots (15)$$

which determines the radius of the boundary. If  $r_0 \leq r_1$  the flow will be viscous everywhere and equation (8) shows that this will be so for  $r_1 > \sqrt{2}\gamma/\tau_c\rho$ ; if  $r_0 \geq r_2$  the flow will be plastic everywhere and the equations of the last sub-section apply. On the other hand, if  $r_1 \leq r_0 \leq r_2$  there is a transition boundary and (15) together with (3) and (9) show that

$$-u_1 \leq \frac{\gamma}{2\eta_0\rho} \frac{a\rho^{\frac{3}{2}}}{(1-\rho)^{\frac{3}{2}}}, \quad \dots\dots (16)$$

where  $a = \sqrt{2}(3/4\pi)^{\frac{1}{2}}\tau_c/2\gamma n^{\frac{3}{2}}$  is the parameter defined previously. Practical values of  $a$  lie in the neighbourhood of unity, so that for  $\rho < 0.99$  a comparison with equation (11) shows that the velocity when any part of a compact flows viscously is less than 1% of the initial velocity when the flow is fully plastic. The neglect of the initial viscosity therefore seems justified.

Using the equation of energy as in the previous sub-sections, the condition that the flow shall be fully plastic is found to be

$$1 - a \frac{(1-\rho)^{\frac{3}{2}}}{\rho^{\frac{3}{2}}} \left[ \ln \frac{1}{(1-\rho)} + \frac{\eta_\infty}{\eta_0} \frac{1}{1-\rho} \right] \geq 0. \quad \dots\dots (17)$$

This corresponds to equation (12) expressed in terms of  $\rho$ . The additional term involving  $\eta_0$  has the same sign as the logarithmic term, so that the curve defining the transition to mixed flow lies very slightly above the curve drawn in Figure 4, except for values of  $\rho$  very close to unity, where the new curve rises to infinity. This rise simply means that when  $\rho$  is very close to unity the flow at the outer boundary always becomes slow enough for an outer region to be viscous. Thus the previous discussion of Figure 4 applies unchanged except that there is always mixed flow ultimately, and sometimes it can become plastic again before the final mixed flow. Further, the barrier can always be penetrated slowly since the flow is partly viscous in this region.

(vi) *Comparison of Theory with Experiment*

It is to be expected that the viscous solid model will explain the sintering of glass, but there appear to be no data on the increase in density of glass compacts as a function of the time of sintering.

It is possible to explain the experiments of Shaler and Udin discussed in § 4 (i) if it is supposed that at high temperatures copper behaves like a Bingham solid, and a rough estimate can be made of the yield stress  $\tau_c$  by using the data for these experiments.

In Udin's wire-pulling experiments the greatest simple tension that was applied to the wires of  $36 \mu$  radius was  $8.1 \times 10^5$  dynes/cm<sup>2</sup>; when corrected

for the surface tension stress this corresponds to an octahedral shear stress of  $2.0 \times 10^5$  dynes/cm<sup>2</sup>. At this stress yield has not occurred and, therefore,  $\tau_c > 2.0 \times 10^5$  dynes/cm<sup>2</sup> at 1,000° c.

Rapid sintering occurred in Shaler's experiments at 850° c., so that the yield stress must have been exceeded. For  $\gamma = 1,500$  dynes/cm. equation (12) leads to  $\tau_c < 2.6 \times 10^5$  dynes/cm<sup>2</sup>. Since the experiments lasted for only a short time, and no large increase in density occurred, the pores would not be spherical. This would increase the pressure due to surface tension by some factor which is probably less than 5. Therefore the yield stress at 850° c. might well be greater than  $2.6 \times 10^5$  dynes/cm<sup>2</sup>.

Shaler found that cylindrical pores drilled in a copper wire did not close when heated to 1,000° c. It follows from equation (13) that  $\tau_c > 0.2 \times 10^5$  dynes/cm<sup>2</sup>; in fact, if  $\tau_c > 2 \times 10^5$  dynes/cm<sup>2</sup> the whole of the wire must have been flowing viscously.

At room temperature the critical shear stress of copper single crystals is  $10^7$  dynes/cm<sup>2</sup>.

#### § 6. THE INFLUENCE OF GAS ON SINTERING

Metals are often sintered in atmospheres of inert gases, and even when the sintering is carried out in a vacuum the pores, once closed, will contain gases evolved from the metal. Sometimes decomposable carbonates are deliberately added to glasses before sintering in order to obtain low-density products with bubble structures.

Gases can affect sintering in two ways (*a*) by their chemical effect on the surface of the powder, or (*b*) by their hydrostatic pressure. Jordan and Duwez (1949) find that copper sinters more quickly in hydrogen than in a vacuum. This is probably due to the reduction of copper oxide on the surface of the powder by the hydrogen. The changes that occur when metal surfaces are heated in inert gases have recently been reviewed by Shuttleworth (1948).

In this paper only the hydrostatic effects of gas pressure will be discussed. The pressure due to surface tension inside a pore of  $30 \mu$  radius is about one atmosphere in the case of copper, so that even a small gas pressure inside the pores will reduce the rate of sintering and may even cause the pores to expand. If  $p$  is the excess of the gas pressure at the surface of the compact over that inside the pores, the rate of sintering when the pores are equal spheres is obtained by replacing  $2\gamma/r$  by  $2\gamma/r + p$  in the expressions for  $u_1$  and  $dp/dt$ . The integrals have only been evaluated for the case of a viscous solid, but the results are qualitatively the same whatever form the equation of mechanical state takes.

The gas pressure inside a pore will vary in a manner that depends on the amount of gas initially present in the pore, the size of the pore and the rate at which it closes. Two cases will be considered in detail: (*a*) a constant pressure difference between the pores and the surface of the compact, and (*b*) a constant mass of gas in each of the pores but no pressure outside the compact.

##### (i) Constant Pressure inside the Pores

If large quantities of gas can dissolve in the metal and the rate of diffusion is large enough to ensure that equilibrium is always maintained between the gas in the pores and that in the metal, or if a reversible chemical reaction involving the gas occurs at the surface of the pores, then the gas pressure inside the pores will remain constant when the size of the pore changes. A constant pressure

difference also occurs when a constant pressure is applied to the surface of the compact and there is no gas pressure inside the pores.

For a viscous solid  $\gamma$  must be replaced by

$$\gamma(1 + pr_1/2\gamma) = \gamma\{1 + b(1 - \rho)^{\frac{2}{3}}/\rho^{\frac{2}{3}}\},$$

where  $b = (3/4\pi)^{\frac{2}{3}}(p/2\gamma n^{\frac{2}{3}})$ , so that instead of equation (10)

$$\frac{\gamma n^{\frac{2}{3}}}{\eta} (t - t_0) = \frac{2}{3} \left(\frac{3}{4\pi}\right)^{\frac{2}{3}} \int_1^{\rho} \frac{d\rho}{(1 - \rho)^{\frac{2}{3}} \rho^{\frac{2}{3}} [1 + b(1 - \rho)^{\frac{2}{3}}/\rho^{\frac{2}{3}}]}. \quad \dots\dots (18)$$

After the substitution  $x^3 = (1 - \rho)/\rho$  the indefinite integral is

$$\frac{2b+1}{b^2+b+1} \frac{1}{2} \ln \frac{1+x^3}{(1+x)^3} - \frac{\sqrt{3} \tan^{-1}(2x-1)/\sqrt{3}}{b^2+b+1} - \frac{3b^2}{b^3-1} \ln \frac{1+bx}{1+x}.$$

In Figure 5,  $\rho$  is shown as a function of the reduced time,  $\gamma n^{\frac{2}{3}}(t - t_0)/\eta$ , for a

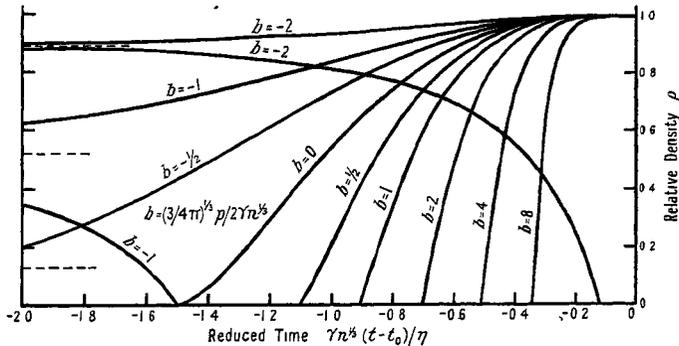


Figure 5 The relative density of a compact as a function of the reduced time when various constant pressures are applied inside the pore, or outside the compact, and the real material behaves like a viscous solid

number of values of the parameter  $b$ . The zero of time has been chosen so that  $t = t_0$  when  $\rho = 1$ ; when the curves are used to predict the behaviour of a compact the zero is decided by the initial density of the compact. The parameter  $b$  is proportional to the pressure difference  $p$  between the pores and the outside of the compact; when  $b = 1$ ,  $n^{\frac{2}{3}} = 100 \text{ cm}^{-1}$  and  $\gamma = 1,500 \text{ dynes/cm.}$ ,  $p = 0.5$  atmosphere. Positive  $b$  corresponds to an externally applied pressure and negative  $b$  to a pressure inside the pores.

For  $b$  positive the compact sinters to unit density in a finite time and the application of a few atmospheres pressure to the outside of the compact reduces the time of sintering to about one-quarter of that required when no pressure is applied. An even more rapid increase in the rate of sintering might be expected if a few atmospheres pressure were applied to the outside of a compact of a material for which the equation of state is similar to that for a Bingham solid. In particular, if the parameter  $a$  is large it should be possible to prevent the increase of density from stopping at some finite value less than the theoretical density.

When  $b$  is negative there is a critical density at which the pressure of the gas inside the pores just balances the surface tension. This occurs when  $-p = 2\gamma/r_1$ , and the corresponding critical density can be calculated from equation (9). When the initial density is greater than the critical density the pressure due to surface tension always overbalances the gas pressure, and sintering to unit relative density occurs in a finite time. On the other hand, when the initial density is

less than the critical density the pores expand and continue to do so at an ever increasing rate. However, the density will never decrease as rapidly as shown in Figure 5; for the expansion will be controlled by the rate at which gas can diffuse into the pores and the later stages of the expansion will take place more as though there were a constant mass of gas in the pores.

(ii) *Constant Mass of Gas inside each Pore*

If an inert gas such as nitrogen is trapped in a compact during pressing it will not dissolve or diffuse appreciably during sintering and the mass of gas inside each pore will remain constant. The pressure exerted by such gas will vary inversely as the volume of the pore, and always opposes the pressure due to surface tension ( $p$  is always negative).

For a viscous solid  $\gamma$  must be replaced by

$$\gamma(1 + p_0 r_0^3 / 2\gamma r_1^2) = \gamma \{1 + C\rho^{\frac{2}{3}} / (1 - \rho)^{\frac{2}{3}}\},$$

where  $r_0$  and  $p_0$  are respectively the initial radius of the pores and the initial pressure inside the pores and

$$C = \left(\frac{4\pi}{3}\right)^{\frac{2}{3}} \frac{p_0}{2\gamma n^{\frac{2}{3}}} nr_0^3.$$

Then instead of equation (10)

$$\frac{\gamma n^{\frac{2}{3}}}{\eta} (t - t_0) = \frac{2}{3} \left(\frac{3}{4\pi}\right)^{\frac{2}{3}} \int^{\rho} \frac{d\rho}{(1 - \rho)^{\frac{2}{3}} \rho^{\frac{2}{3}} [1 + C\rho^{\frac{2}{3}} / (1 - \rho)^{\frac{2}{3}}]}. \quad \dots (19)$$

After the substitution  $x^3 = (1 - \rho) / \rho$  the indefinite integral is

$$\begin{aligned} & -\frac{C-1}{C^3+1} \frac{1}{2} \ln \frac{1+x^3}{(1+x)^3} - \frac{C+1}{C^3+1} \sqrt{3} \tan^{-1}(2x-1) / \sqrt{3} \\ & + \frac{C^2}{C^3+1} \frac{1}{2} \ln \frac{x^2+C}{(1+x^3)^2} - \frac{3(-C)^{\frac{1}{2}}}{C^3+1} \ln \frac{x - (-C)^{\frac{1}{2}}}{x + (-C)^{\frac{1}{2}}} \end{aligned}$$

for  $C$  negative.

In Figure 6,  $\rho$  is shown as a function of the reduced time,  $\gamma n^{\frac{2}{3}}(t - t_0) / \eta$  for a number of values of the parameter  $C$ ; the zero of time has been chosen so that  $t = t_0$  when  $\rho = 0$ . When these curves are used to predict the behaviour of a particular compact, the value of  $C$  is determined by the initial pore radius and initial gas pressure, and the zero of time is specified by the initial density. The parameter  $C$  is proportional to the initial pressure inside the pores; when  $C = -1$ ,  $n^{\frac{2}{3}} = 1/r_0 = 100 \text{ cm}^{-1}$  and  $\gamma = 1,500 \text{ dynes/cm.}$ ,  $-p_0 = 0.1$  atmosphere.

Corresponding to any initial mass of gas inside each pore, there is an equilibrium pore radius at which the gas pressure just balances the pressure due to surface tension; this occurs for  $r_1^2 = -p_0 r_0^3 / 2\gamma$ , and the equilibrium density is found from equation (9). The density of a compact approaches the equilibrium density asymptotically; it decreases or increases according as the initial density is greater or less than the equilibrium density.

It has been seen that very small gas pressures can have quite large effects. When the pores are not all equal in size, or the mass of gas in each is not proportional to the initial pore volume, then the behaviour of any individual pore may be anomalous. In particular, suppose that some soluble gas such as hydrogen exerts a constant pressure  $p$  inside all pores and that the pores are of various sizes,

then the larger pores for which  $2\gamma/r < p$  will expand while the smaller pores will contract. Thus great care is needed in interpreting experimental results concerning the change in size distribution of pores during sintering.

§ 7. ATOMIC MECHANISMS IN SINTERING

A complete description of the atomic processes by which the deformation of metals occurs during sintering must await further experiments. However, the speed with which deformation occurs and the presence of a yield point indicates that a dislocation mechanism is probably operative. The yield point may possibly be due to dislocations breaking away from atmospheres of solute atoms which lock them (Cottrell 1948, Cottrell and Bilby 1949); this would imply a temperature-sensitive yield point.

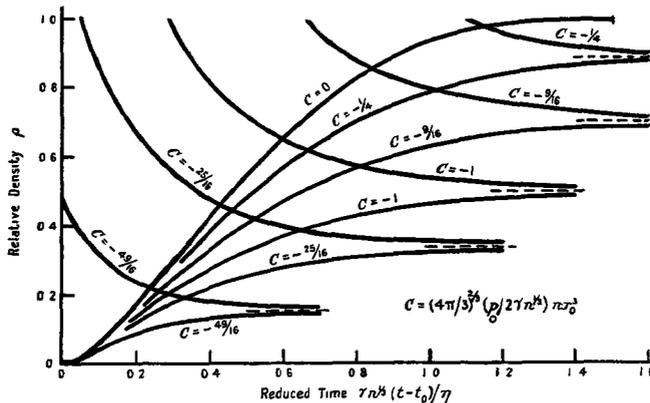


Figure 6. The relative density of a compact as a function of the reduced time when there is a constant mass of gas inside each pore and the real material behaves like a viscous solid.

The fact that deformation is caused by the change in surface energy puts a restriction on the possible modes of deformation. Deformation cannot occur by a series of catastrophic processes in each of which one block of the crystal is rapidly displaced with respect to another, since this would increase the surface area by the formation of slip lines. In order that appreciable rumpling of the surface shall not occur, the rate of deformation must be slow compared with the rate at which rearrangement of the surface atoms can take place by means of surface and volume diffusion. Hansen (1939) has shown that slip lines do not appear on the surface of aluminium when it creeps at high temperatures.

Shuttleworth (1949 b) has discussed the distinction between the surface free energy and the surface tension of solids. These are equal only when the surface energy is independent of the strain, a condition which does not, in general, hold for solids.

§ 8. SUGGESTED EXPERIMENTS

The theory developed in this paper connects the rate of increase of density during sintering with the mechanical properties of the bulk material. There are no adequate experimental data on either of these aspects of the theory, and some experiments which could usefully be carried out are suggested in the following paragraphs.

There is a need for experiments which determine the laws of deformation of materials at sintering temperatures and under small stresses of a few atmospheres

or less. The rate of shear strain should be determined as a function of the shear stress. This would decide whether or not metals have a yield point at low stresses, and whether or not there exists a simple equation of mechanical state in which the rate of shear strain depends only on the shear stress and the temperature. These experiments should also be of importance for suggesting the mechanisms by which deformation takes place at sintering temperatures.

There is also a need for experiments which determine the density of a powder compact as a function of the pore size, the time and the temperature. These experiments could most usefully be done with glass which behaves as a homogeneous viscous solid, and with silver for which there would be no complications due to oxide films. The experiments should be carried out in a vacuum and the particles used should be equal spheres and thoroughly degassed.

It would be interesting to see if the results of applying small external pressures to a compact are in agreement with the predictions of the theory.

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