Chapter 4

THERMOMECHANICS OF POWDER COMPACTION
AND MASS MIXING

The previous two chapters presented certain fundamentals of shock waves and the shock compression technology. We found that the uniqueness of shock compression comes from the interdependence of shock transition and material properties. That is, shock loading conditions cannot be determined independently of material response behavior, which in turn is affected by the process of shock transition. To illustrate this interdependence, we considered two idealized models of dense solids as representative examples.

The most interesting media, from an industrial application point of view, are powders, i.e., low density compacts composed of powder particles. Therefore, in this and the subsequent chapters, we shall extend shock wave analysis to such media again using first order models. In Chapter 4 we shall be concerned with the compaction of powders and will address the question of heterogeneous processes. But, the study will be limited to problems that do not require extensive calculations. Emphasis is placed on model systems. Chapter 5 is concerned with chemical reactions in powder mixtures. Chapter 6 will examine computational modeling and its applications to the study of plane shock propagation in a variety of reactive powder mixtures, and the analysis of experiments, in which samples are preserved for post shock analysis.

4.1 A One Dimensional Particulate Model

In this section we present a particulate model of shock wave propagation in a powder assemblage to highlight discreteness of such a medium. This model is an adaptation of the model proposed by Lotrich et al. (1986) and Thouvenin (1965).

Let a powder material be represented by smooth disks threaded periodically on a "string", having mass $m$, unit cross-section, thickness $d$, and separation $l$ as shown in Fig. 4-1. A shock wave is generated in this system by abruptly moving one particle with infinite mass (a rigid wall) to the right with a constant velocity
$u$. This type of shock wave is commonly seen on a highway when a heavy truck ploughs from behind into a string of small cars.

For the sake of illustration, we shall first examine the case in which the disks are assumed to be rigid. Later, it will be modified to allow permanent deformations. Upon impact of disk 0 on disk 1, the latter begins to move with the velocity $2u$ (not $u$! See Eq. (135) in chapter 2. Subsequently, disk 1 impacts disk 2 at time $l/2u$ and stops. Now disk 2 moves with velocity $2u$ and impacts disk 3 at time $2(l/2u)$. And so on. Such “go-stop” motions of disks may be best illustrated if the motions are traced in a position-time plane as shown in Fig. 4-2. It may be seen from the figure that the front of the disturbance propagates $n(l + d)$ in time $(l/2u)$. Hence the “shock” velocity is
\[ U = \frac{n(\ell + d)}{n(\ell/2u)} = 2u \left( 1 + \frac{d}{\ell} \right) \]  

(1)

Since \( l/(l + d) \) can be regarded as the "porosity" of the particle assemblage \( \Phi \), Eq. (1) can be written as

\[ U = \frac{2u}{\Phi} \]  

(2)

Tracing the trajectory of disk 1, one can deduce from the figure that the average particle velocity of the medium is \( u \), the piston velocity.

Other variables of interest, such as density and pressure changes, can be calculated as follows. At time \( t \), the shock wave has set in motion \( n \) disks where

\[ n = \frac{U t}{(\ell + d)} \]  

(3)

Since the wall also moves to the right with the velocity \( u \), these disks are compressed into distance of \((U - u)t\). Therefore, the density (linear) is given by

\[ \rho + \frac{mn}{(U - u)t} = m \frac{U}{(\ell + d)} \frac{U}{(U - u)} = \rho_0 \frac{U}{(U - u)} \]  

(4)

This is precisely the jump condition for mass conservation.

Pressure and internal energy changes are found from the linear momentum and power relationship as follows.

\[ p = mu \frac{U}{(\ell + d)} = \rho_0 u U \]  

(5)

\[ pu = m \left( \frac{1}{2} u^2 + \Delta E \right) \frac{U}{(\ell + d)} = \rho_0 \left( \frac{1}{2} u^2 + \Delta E \right) U \]  

(6)

where \( \Delta E \) represents the internal energy change associated with particle velocity fluctuation. Now it can be shown from Eqs. (2), (5) and (6) that

\[ \Delta E = \frac{1}{2} u^2 \]  

(7)
\[ p = \frac{2\rho_0 u^2}{\Phi} \]  

(8)

Equation (7) indicates the equipartition of energy.

Thus, the above described model has all the important features of shock wave propagation we have seen in Chapter 2. But, it also exhibits peculiar behaviors that arise as a result of the assumptions involved. For instance, the assumption of rigidity leads to the result that \( U \to \infty \) as \( \Phi \to 0 \). That is, the shock wave in the disks is assumed to propagate at infinite speed. Obviously, the model cannot deal with important mechanisms such as plastic deformation and surface heating.

Short of numerical simulation, a simple model such as the above cannot and should not address all the aspects of powder consolidation under shock loading. The model is intended to be a pedagogical analogue to capture a few mechanistic aspects of shock propagation in powder assemblages. In this spirit, however, we can extend the above model so that it has proper limits as \( \Phi \) goes to zero.

To this end we introduce two regimes of internal motions during the propagation of a shock in the particle assemblage. The first is the motion of a shock wave through a disk, and the second is the surface motion as the shock reaches the right-hand end of the disk. We assume the latter to be twice the particle velocity induced in the disk. Then, we can equate the overall motion to the internal ones through the relationships,

\[ \frac{\ell + d}{U} = \frac{d}{U_s} + \frac{\ell}{2u_s} \]  

(9)

\[ \frac{\ell + d}{U} = \frac{d}{u_s} + \frac{\ell}{2u_s} \]  

(10)

where "s" signifies the quantities associated with the internal motions. These equations have correct limits as \( l \to 0 \). In fact, the right-hand quantities can be thought of as lower limits of the left-hand sides. Then, rearranging terms in Eqs. (9) and (10) one finds,

\[ u = \frac{2u_s}{2 - \Phi} \]  

(11)

\[ U = \frac{2u_s U_s}{2u_s (1 - \Phi) + \Phi U_s} \]  

(12)
The changes in pressure, internal energy, and density can be shown to be identical to Eqs. (5), (7), and (4) respectively. However, we cannot use Eq. (8) for pressure, because it is based on Eq. (2), which is no longer valid. However, since \( U_s \) and \( u_s \) are the properties of the solid constituent we may assume a linear \((U_s - u_s)\) relationship. Then, Eq. (5) yields

\[
p = \frac{\rho_{s0}u^2(1 - \Phi)(1 - 0.5\Phi)[C_0 + s(1 - 0.5\Phi)\mu]}{(1 - \Phi)(1 - 0.5\Phi)\mu + 0.5\Phi[C_0 + s(1 - 0.5\Phi)\mu]}
\]  

(13)

where \( U_s = C_0 + su_s \).

According to Lotrich et al. (1986), model calculations for several metals are in agreement with experimental results as shown in Fig. 4-3; but, this agreement may be the result of the coordinates chosen. For instance, Eq. (12) shows that when \( u = 0 \), then \( u_s = 0 \) and \( U = 0 \). This behavior is expected from the model, but is still an undesirable result, because sound waves do propagate even in powders (Watt et al., 1976).

The calculation of density with the linear \( U_s - u_s \) relation also shows an anomalous behavior. With

\[
\frac{\rho}{\rho_0} = \frac{(2 - \Phi)[C_0 + s(1 - 0.5\Phi)\mu]}{(1 - \Phi)[2C_0 + 2s(1 - 0.5\Phi) - (2 - \Phi)\mu]}
\]  

(14)

when \( u = 0 \), Eq. (14) becomes

\[
\rho = \frac{(2 - \Phi)}{(2 - 2\Phi)}\rho_0 = (1 - 0.5\Phi)\rho_{s0}
\]

where \( \rho_{s0} \) = the initial solid density.

This means that the powder restacks to a new density for any infinitesimally small pressure—akin to the behavior of an ideally-locking solid which compresses to the solid density at any positive pressure. We shall return to some aspects of this behavior in the next section.

Equation (13) represents the powder Hugoniot in the \((p - u)\) plane in terms of the Hugoniot of its constituent solid. Unfortunately, the expression is too complex to see its characteristic features without detailed analysis, although the jump conditions themselves reveal some physical trends without involving analysis. For example, according to the momentum and mass conversation equations
Fig. 4-3. A comparison of the ideally-locking solid with experimental results for AlN powder.

\[ p = \frac{u^2}{V_0 - V} \]

This immediately shows that for any given \( u \), the Hugoniot pressure is much lower than that in the solid of the same material. Thus it is very difficult to develop a very
high pressure shock in low density powders. As will be discussed in Chapter 6 on the numerical simulation of shock-induced chemical reactions, the magnitude of pressure discontinuity may play a significant role in their initiation.

Also, it may be easily seen from Eqs. (5) and (6) that the internal energy change is the Hugoniot equation,

\[ \Delta E = E - E_0 = \frac{1}{2} \rho (V_0 - V) \]

However, it is important to note that \( V_0 \) is the initial powder volume, and that it is much greater than the volume of its solid constituent. Therefore, if the compaction is irreversible under shock loading, then a large temperature rise is expected from void collapse.

If the shocked state in powder is assumed to be an homogeneous equilibrium state, then the temperature calculation can be carried out using the techniques discussed in Chapter 2. However, it is unlikely that such an assumption is valid for an inherently heterogeneous medium such as powder, particularly during the initial phase of shock compression. Therefore, the subject of heterogeneous heating in powders will be treated separately in Section 4.3.

4.2 Continuum Models

The term “continuum” is used in the sense that response behavior of a powder or a porous material is fully determined by macroscopic variables such as stress, strain, and internal energy. In this section, the state of these variables is assumed to be homogeneous and the question of heterogeneous energy deposition will be addressed in the next section.

Broadly speaking, continuum modes can be classified into two categories.

1. Hydrodynamic models.
2. Models with shear effects.

There are many sub-categories of the first type, ranging essentially from ad-hoc models to models that reflect micro-mechanics of pore collapse. Early models of this type were developed mostly for porous materials and are concerned with the description of their incomplete compaction at moderate pressures (several GPa). These materials often exhibit a small, but finite strength, while powders show very little shear strength. By contrast, there appears to be only one type in the second category that belongs to the continuum plasticity theory (CPT). Models of this type are widely used in the description of soils and other geological materials.

The aim of this section is an heuristic discussion of prevailing concepts which are applicable to shock compression of porous and powder materials. Although the response of powders has features that are different from those of porous materials, we will not make any distinction.
4.2.1 Hydrodynamic models

If the dynamic response of a powder can be characterized by a continuum model whose properties are determined by quantities such as pressure and internal energy in some averaged sense, then the Hugoniot of this material is governed by the same equation as that for a solid material,

$$
\left( \frac{dp}{dV} \right)_{H} = \frac{\left( \frac{\partial p}{\partial V} \right)_{s} + \frac{\gamma}{2V} (p - p_{0})}{1 - \frac{\gamma}{2V} (V_{0} - V)}
$$

(15)

An additional assumption needed is that the specific internal energy of the powder is the same for the solid material.

Likewise, the jump conditions are given by

$$
\rho_{0} U = \rho (U - u)
$$

(16)

$$
p = \rho_{0} u U
$$

(17)

$$
E - E_{0} = \frac{1}{2} p (V_{0} - V)
$$

(18)

What is unique about powders is that $V_{0}$ is now an adjustable parameter. Then, by inspection of Eq. (15) we see immediately that beyond a certain critical value of $V_{0}$, slopes of the Hugoniot become positive: the density decreases as the pressure increases. At very high pressures, the behavior of the Hugoniot will be further complicated because of large increases in the internal energy (Kormer et al., 1962). However, these issues will not be addressed in this section.

Broadly speaking, there are two types of models used to describe shock response of powders at moderate pressures. The first category is concerned only with the equation of state of completely compacted powders, and the second with the relationship for pore collapse.

First we begin with two examples of the first category. The simplest of them is called the "ideally-locking solid" or "snow plow" model (Salvadori, Skalak, and Weidlinger, 1960). This model assumes an incompressible solid constituent and complete compaction for $p > 0$. Then putting $V = V_{s0}$ in Eqs. (16)–Eq. (18), one obtains

$$
p = \frac{u^{2}}{(V - V_{s0})}
$$
U = V_0 \left( \frac{P}{V - V_{s0}} \right)^{\frac{1}{2}}

Figure 4-4 shows a comparison of the model prediction with experimental data for AIN. The observed agreement may mean that the $p-u$ curve is relatively insen-

Fig. 4-4. Predictions of the Snow-Plow model and experimental data for AIN.
sitive to pore compaction curves. Unloading data in this figure indicates that the state behind the shock front is indeed irreversibly consolidated and begins to exhibit consolidation at pressures above 5 GPa.

Inclusion of the compressibility of solid grains is normally done through the Mie-Grüneisen equation,

\[ p = p_r + \rho \gamma (E - E_r) \]  

(19)

where \( p_r \) and \( E_r \) are the pressure and specific internal energy of a reference state. This means that once consolidated, the compacted material is indistinguishable from the dense solid. Figure 4-5 illustrates two commonly used reference states: Isentropic and Hugoniot curves of the solid constituent. If the former were used, then

\[ E_r = -\int_{V_{s0}}^{V} p_s dV \]  

(20)

where \( V_{s0} \) is the initial specific volume of the solid material. If the latter were used, then

Fig. 4-5. A schematic illustration of the construction of powder Hugoniots based on its constituents solid Hugoniot.
where \( p_r \) can be evaluated using the techniques discussed in Chapter 2. Linear \( U-u \) relationships provide a reasonable approximation for many materials.

For moderate pressures, the quantities in Eqs. (20) and (21) are approximately equal. Hence, the adiabatic Murnaghan equations may be used to evaluate \( E_r \) in Eq. (21) (Butcher and Karnes, 1969; Kondo et al., 1985). If such an approximation is not appropriate, then one can solve Eq. (19) for \( p \) in terms of the solid Hugoniot which in turn satisfies its own jump conditions, Eqs. (15)–(18). With this choice,

\[
p = p_r \left[ \frac{1 - (\rho \gamma)(V_{s0} - V)/2}{1 - (\rho \gamma)(V_0 - V)/2} \right]
\]

where \( p_r \) is the reference solid Hugoniot and given by

\[
p_r = \frac{\rho_{s0} C_0^2 \varepsilon}{[1 - S \varepsilon]^2}
\]

where \( C_0 \) and \( S \) are the coefficients of the linear \( U-u \) relationship for the solid and \( \varepsilon = 1 - \rho_{s0}/\rho \). If the compression of the solid is small so that \( \varepsilon \ll 1 \), then the second term in the numerator of Eq. (22) can be approximated by one. Then, to the first order in \( \varepsilon \),

\[
p \approx \frac{2p_r/\gamma}{2/\gamma + 1 - \rho/\rho_0}
\]

Since for metals such as Al, Cu, and Ni, \( \gamma \) is 2, Eq. (24) becomes a simple expression,

\[
p \approx \frac{p_r}{2 - \rho/\rho_0}
\]

Simons and Legner (1982) further simplified Eq. (24) by noticing that the thermal energy due to pore collapse is the dominant term in the equation of state, and that the reference state may be taken along an isentropic “cold” compression curve expanded about the initial solid density. That is,
\[ p_r \approx \frac{\rho - \rho_{s0}}{\rho_{s0} K_s} \quad (25) \]

\[ E_r \approx \left( \frac{\rho - \rho_{s0}}{2 K_s \rho_{s0}^3} \right)^2 \quad (26) \]

Then substituting Eq. (25) into Eq. (24) solving for \( \rho \), one obtains

\[
\rho = \frac{1 + \left( 1 + \frac{\gamma}{2} \right) K_s p}{\rho_{s0} \left( 1 + \frac{\gamma}{2 \Sigma} K_s p \right)}
\]

where \( \Sigma = \rho_0 / \rho_{s0} \).

The threshold condition for anomalous Hugoniot is the same for Eqs. (15) and (22).

\[
\Sigma = \frac{\rho_0}{\rho_{s0}} = \frac{\gamma}{2 + \gamma}
\]

For metals which have a Grüneisen constant of about 2, this occurs at 50% solidity for the starting powder. Figure 4-6 shows two selected examples taken for Simons and Legner (1982). Agreement is remarkably good in view of the drastic approximations involved.

Recently, however, Oh and Persson (1989) showed that the constant volume extrapolation used in the above models is not reliable. They proposed a new extrapolation at constant pressure such that

\[
\left( \frac{\partial E}{\partial V} \right)_p \approx \left( \frac{\partial E}{\partial V} \right)_{Hugoniot}
\]

Figure 4-7 shows their comparison of the two model predictions with experimental results for copper powder. In this calculation, the constant volume extrapolation is based on Eq. (19) with a constant \((\gamma/V)\). The improved accuracy of the new model for highly porous copper is evident.

The procedure for evaluating the shock temperature in powders is the same as that for dense solids. For instance, using the isentrope as the reference curve,
Fig. 4-6. Hugoniots of selected porous materials using one of the schemes illustrated in Fig. 4-5 (after Simons and Legner, 1982).

one obtains

\[ E = \frac{1}{2} p(V_0 - V) = -\int_{V_0}^{V} p_s dV + \int_{T_s}^{T} C_v dT \]  
(29)

\[ T_s = T_0 \exp \left( -\int_{V_0}^{V} \frac{\gamma}{V} dV \right) \equiv T_0 \exp \left[ -\left( \frac{\gamma}{V_0} \right) (V - V_0) \right] \]  
(30)
Fig. 4-7. A comparison of model calculations with experiments. Solid lines are based on the Oh-Persson equation and broken lines on the Mie-Grüneisen equation (see Eq. (8)).

For porous materials, shock heating comes mostly from the collapse of pores. Hence, the following simple estimate serves as a reasonable first order approximation.

\[
\Delta T \approx \frac{pV_0 \Phi_0}{2C_V}
\]  

where \( \Phi_0 \) is the initial porosity \((1-\rho_0/\rho_0)\). Geometrically, the quantity is the triangular area connecting the three points \( V_0, p, \) and \( V_{s0} \) as shown in Fig. 4-8. This area is much greater than the triangular area \( V_{s0}, p \) and \( V \). Then, within the imposed assumptions, the temperature increase is a linear function of pressure. Figure 4-9 shows two representative examples of Eq. (31). For reference, the melting temperature of the material at atmospheric pressure is also indicated in the figure.

Residual temperature in shock-loaded powders may again be calculated using the procedure for dense solids, but a more expedient approach is to ignore the change due to adiabatic unloading. If the powder is consolidated to a solid, and unloads along its adiabatic, then the adiabatic temperature drop is of the same order as that ignored in Eq. (31). This means that as an estimate for residual temperatures, Eq. (31) should be better than that for the shock temperature, provided that the material will remain in the same phase.

We shall now consider the second category: models of pore-collapse.
Fig. 4-8. A schematic illustration of energy dissipation in shock compression of porous and powder materials.

Fig. 4-9. Temperature increases in shock compression of porous Ni and Al for three initial porosities. The initial temperatures of Ni and Al are set at room temperature.
Broadly speaking, there are also two kinds of models. The first is empirical ones, and the second is based on some mechanistic interpretation of pore-collapse mechanisms.

One example of the empirical type is that of Raybould (1975). He showed that Eq. (32) represents the experimental relationship for Al and Fe powders reasonably well.

\[ \rho = \rho_0 \left( a + \frac{1 - a}{1 + bp} \right)^{-1} \tag{32} \]

where \( a = \rho_0 / \rho_s \) and \( b \) represents the stiffness of the powder. The resulting \( p-u \) relationship is given by

\[ u^2 = \frac{(1 - a)bp^2}{\rho_0 (1 + bp)} \]

According to Eq. (32), \( \rho \) asymptotically approaches the solid density \( \rho_s \) as \( p \) goes to infinity. This means that solid grains are assumed to be incompressible. The model was not concerned with the question of unloading, but was developed to find a mathematical fit to experimental Hugoniot data.

Raybould’s calculation of the average temperature rise is based on the area under the compression curve, Eq. (32), rather than the energy given by the jump condition. The result is

\[ \Delta T = \frac{(1 - a)}{a \rho_s c_p b} \left[ \ln(1 + P) - \frac{P}{1 + P} \right] \]

where \( c_p \) is the specific heat of the solid and \( P = bp \).

A systematic development of the phenomenological model called “the \( p-\alpha \) model” was carried out by Hermann (1969). In this model pore collapse is described by introduction of the distention parameter \( \alpha \) defined by

\[ \alpha = \frac{V}{V_s} \tag{33} \]

where \( V \) is the specific volume of the porous material and \( V_s \) that of the solid constituent. \( V_s \) is not assumed to be incompressible. In addition Hermann suggested that the volumetric response of the solid constituent is unaffected by the presence of the pores and that specific internal energy is the same for the porous
and the solid materials. Mathematically, the assumption was expressed as

\[ p = f(V_s, E) \]

where \( p \) is the pressure for the porous material and \( f \) the EOS function for the solid constituent. Later this was modified by Carroll and Holt (1972) to accurately account for the effect of stress averaging to

\[ p = \alpha^{-1} f(V/\alpha, E) \]  \hspace{1cm} (34)

where \( f \) is still the equation of state function for the solid constituent.

In the Hermann’s model, the \( p–\alpha \) relationship consists of both the elastic and plastic response behaviors. The elastic behavior is formulated using a sound speed relationship.

\[ C^2 = -V \left( \frac{\partial p}{\partial V} \right)_s \]

Substituting Eq. (34) into this definition, one obtains

\[ C_t^2 = C_s^2 \left[ 1 + \frac{d\alpha}{dp} \left( K_s0 - \frac{p}{\alpha} \right) \right]^{-1} \]

where the subscripts “t” and “s” are porous and solid materials, respectively. For small pressures, \( (p/\alpha) \ll K_s0 \),

\[ \left( \frac{d\alpha}{dp} \right)_{elastic} = \frac{1}{K_s0} \left[ \left( \frac{C_t}{C_s} \right)^2 - 1 \right] \]

\( C_t \) can be modeled theoretically (e.g., Watt et al., 1970), but Hermann proposed a computationally convenient empirical approach in which it is assumed to change linearly from \( C_{t0} \) to \( C_{s0} \) as \( \alpha \) varies from \( \alpha_0 \) to one.

\[ \left( \frac{C_t}{C_s} \right) = 1 + \frac{1 - \alpha}{1 - \alpha_0} \left( \frac{C_{t0}}{C_{s0}} - 1 \right) \]

where “0” signifies values at zero pressure.
The description of plastic response in the original model is an empirical one based on a polynomial function in $p$. An especially simple case found adequate by Butcher and Karnes (1969) for porous iron is

$$\frac{x - 1}{x_e - 1} = \left(1 - \frac{p - p_e}{p_{cr} - p_e}\right)^2 \quad (35)$$

where $p_{cr}$ represents the pressure at which pore collapse is complete and $x_e$ and $p_e$ the elastic limit. Other functional forms and their rationals are reviewed in Cowin and Carroll (1976). There are also models that consider effects such as strain hardening and rate effects (e.g., Carroll and Kim, 1984; Carroll and Holt, 1972; Butcher, Carroll, and Holt, 1974).

Figure 4-10 shows a schematic of the $p$--$x$ model in which $p_e = 0$ and unloading from an incomplete pore collapse is drawn to insure a smooth transition near the initial state, $x_0$. Analytically, such a transition may be accomplished by the relationship

$$x_{un} = \xi x^* + (1 - \xi) x(p)$$

where $x^*$ is the minimum $x$ attained before unloading and

$$\xi = \frac{x^* - x_0}{1 - x_0}, \quad 1 \leq x^* \leq x_0$$

The strength of the $p$--$x$ model is that it allows, in a simple mathematical

![Figure 4-10](image_url)
form, a detailed description of irreversible compaction behavior at low pressures and reduces to the correct Hugoniot at high pressures. Once the pore compaction curve is determined at one initial porosity, the model predicts the response at other initial porosities. Because of these features, the model has been widely used in numerical work on shock propagation in porous media. However, as with any empirical model, an important quantity such as the crush-up pressure must be determined experimentally. To predict such a value, or even the trend, we need mechanistic models that are based on the actual internal mechanisms of grain deformation.

There are two prevailing viewpoints as to solving the problem. The first views powders as an assemblage of idealized particles in contact and the collapse of voids is considered through the deformation and packing configuration of the contact areas. Pore size distribution may be included by means of statistical averaging. The question of cohesion is not considered in these models. The second approach is to replace the response of a particle assemblage with that of an equivalent single grain (e.g., a hollow sphere). This is a particularly useful picture of a continuous solid with many voids. For powders, however, early stage deformations are probably best described by contact-point models, while late stage deformations may be better represented by the second view. An illustration of the transition from ‘contact points deformation’ to ‘deformation of voids in a matrix’ is shown in Fig. 4-11. Nevertheless, in numerical calculations equivalent sphere models have been successfully used for the entire regime of pore compac-

![Diagram of pore compaction](image)

Fig. 4-11. An illustration of the three stages of quasi-static powder compaction. Initial restacking eliminates particle bridging. At higher pressures particle deformation becomes the dominant model of compaction.
We shall consider one basic model from each of the two mechanistic viewpoints.

1) Plastic deformation at contact points (Fischmeister and Artz, 1983)

In reference to Fig. 4-11, assume that the model material consists of spherical particles of radius \( R \) and each particle has \( Z \) contacts on average, and that the applied pressure and the forces opposing it are in static equilibrium. The force equilibrium may be written as

\[
f = \frac{4\pi R^2}{ZD} p \tag{36}
\]

where \( f \) is the resistive force across a contact point (or an area) and \( D \) the relative density. The physical meaning of this expression is that the average contact force is the pressure times the average contact area. If we model \( f \) on the basis of a spherical indenter entering a flat plate, then

\[
f = 3\sigma_y a \tag{37}
\]

where \( \sigma_y \) is the flow stress of the material and \( a \) the contact area. Putting Eq. (37) into (36) yields

\[
p = \frac{3}{4\pi R^2} \sigma_y a Z D \tag{38}
\]

where all the terms involved are assumed to be functions of \( D \).

By an appropriate choice of these functions, Fischmeister and Artz (1983) were able to obtain reasonable agreement between the theoretical prediction and experimental data for bronze powder. See Fig. 4-12. A small difference was observed when \( D > 90\% \) was attributed to the transition from the contact point deformation to the void collapse in the matrix.

In the region of high relative density, they proposed a linear combination of two mechanisms described by

\[
p = \sigma_y \left[ \frac{3}{4\pi R^2} a Z D f_s + 2 f_h M \left( \frac{a(1)Z(1)}{(a(1)Z(1) - a(D)Z(D))} \right) \right] \tag{39}
\]

where \( f \) indicates the volume fraction of materials deforming in each mode and \( f_s + f_h = 1 \). The second term is based on the widely used relationship
Fig. 4-12. Compaction of spherical bronze powder and predictions of the particle-in-contact model. (after Fischmeister and Artz (1983)). Broken line is the prediction based on Eq. (24) and solid line Eq. (25). Open circles are data from die compaction and dark circles are isostatic compaction data.

\[ p = K \epsilon n \frac{1}{(1 - D)} \]  \hspace{1cm} (40)

where \( K \) can be related to the yield strength of the material as discussed in the next section. To our knowledge, these equations have not previously been used for applications in shock wave propagation. However, they offer an interesting alternative to the second view which is concerned with only void space and ignores particles-in-contact aspects of a particle assemblage. The discussion of bonding needs the alternative viewpoint.

2) Hollow sphere model (Carroll and Holt, 1972)

Figure 4-13 shows schematically the central idea of this model, namely that the hydrodynamic pore compation of a ductile powder can be effectively described by that of a single hollow sphere subjected to pressure on its outer

Fig. 4-13. A hollow sphere model of pore collapse.
boundary while the inner boundary remains free.

Apparently, Torre (1948) was the first to use such a model to interpret a widely used empirical equation,

\[ p = A + B \ln \frac{1}{(1 - D)} \]  

(41)

where \( D \) is the relative density. The solid material is assumed to be a rigid-plastic material. Carroll-Holt (1972) generalized the analysis in the preview of the \( p-\alpha \) model and successfully applied it to shock propagation in porous aluminum. Later with Butcher (1974), they extended the theory to include a dissipative mechanism.

In what follows, we highlight selected aspects of the basic static model. For details and other developments, the readers are referred to the original papers.

Let us assume that the solid constituent is homogeneous and isotropic. Then, the basic static equations of a hollow sphere subjected to pressure on its outer boundary consist of the following four sets of equations.

(1) The radial equation of equilibrium

\[ \frac{d\sigma_r}{dr} + \frac{2}{r}(\sigma_r - \sigma_\theta) = 0 \]  

(42)

where \( \sigma \) is the radial coordinate, and \( \sigma_r \) and \( \sigma_\theta (= \sigma_\phi) \) are the principal radial and the circumferential stresses.

(2) The boundary conditions

\[ \sigma_r = -p \text{ at } r = b \]  

\[ = 0 \text{ at } r = a \]  

(43)

where \( a \) and \( b \) are the inner and outer radii of the deformed sphere. The relative density \( D \) and its initial value are given by

\[ D = 1 - \frac{a^3}{b^3}, \quad D_0 = 1 - \frac{a_0^3}{b_0^3} \]  

(44)

where "0" denotes the initial values, and \( \alpha \) is related to \( D \) by

\[ \alpha = 1/D \]  

(45)

(3) Kinematic relations

Strain components in the \( r \) and \( \theta \) directions are described by infinitesimal relations.
\[
\varepsilon_r = \frac{du}{dr}, \quad \varepsilon_{\theta} = \frac{u}{r}
\]

(4) Solid behavior: an elastic-perfectly plastic material. Elasticity is described by Hooke’s law

\[
\varepsilon_r = \frac{1}{E} \left[ \sigma_r - 2v\sigma_{\theta} \right]
\]

\[
\varepsilon_{\theta} = \frac{1}{E} \left[ (1-v)\sigma_{\theta} - v\sigma_r \right]
\]

These equations hold until the yield condition (either von Mises or Tresca)

\[
\sigma_r - \sigma_{\theta} = Y
\]

is reached. Plastic deformation of the solid is assumed to be incompressible.

Solutions to the above defined problem depend on the plastic region that begins at the inner boundary and spreads toward the outer boundary. Therefore, there are three solutions depending on the location of the elastic-plastic boundary. The results are

\[
p = \begin{cases}
\frac{4G(\alpha_0 - \alpha)}{3\alpha(\alpha - 1)} \\
\frac{4}{3} G + Y - \frac{2G\alpha_0}{3} + Y\ln\left(\frac{\alpha}{\alpha - 1}\right) + \frac{2G(\alpha_0 - \alpha)}{Y(\alpha - 1)}
\end{cases}
\]

\[
\left\{\begin{array}{c}
\left(\alpha_0 \geq \alpha \geq \alpha_1\right) \\
\left(\alpha_1 \geq \alpha \geq \alpha_2\right) \\
\left(\alpha_2 \geq \alpha \geq 1\right)
\end{array}\right\} \quad (46)
\]

where \(\alpha_1\), and \(\alpha_2\) signify the elastic limit and the onset of fully plastic state, respectively, and \(G\) is the shear modulus of the solid. Their values and the corresponding pressures are given by

\[
\alpha_1 = \frac{2G\alpha_0 + Y}{2G + Y}, \quad p_1 = \frac{2Y}{3\alpha_1}
\]
\[ \alpha_2 = \frac{2G\alpha_0}{2G + Y}, \quad p_2 = \frac{2}{3} Y \ln \frac{\alpha_2}{\alpha_2 - 1} \]

The \( p-\alpha \) relation obtained in Eq. (46) involves only two material constants: the shear modulus \( G \), and the yield strength. Importantly, Carroll-Holt observes (1) that the porosity change in the first two regimes is quite small and (2) that the assumption of plastic incompressibility also has small effect on the behavior of pore compaction. Thus, the process of pore-collapse is dominated by the plastic behavior of the solid constituent. If we exclude early stage behavior, the pressure-porosity relation in simply given by

\[ p = \frac{2}{3} Y \ln \frac{\alpha}{\alpha - 1} = \frac{2}{3} Y \ln \frac{1}{(1 - D)} \]  

(47)

Since in the fully plastic regime \( \alpha_r - \alpha_0 = Y = \text{constant} \), we can obtain the above equation by a direct integration of Eq. (42)

\[ p = 2 \int_a^b \left( \alpha_r - \alpha_0 \right) \frac{dr}{r} = 2Y \ln \frac{b}{a} = \frac{2}{3} Y \ln \frac{1}{(1 - D)} \]

This is the form of the equation used by Fischmeister and Arzt to describe the pore-compaction behavior when \( D > 0.9 \).

Conceptually, the Carroll-Holt model provides a very promising means of calculating the \( p-\alpha \) in terms of material properties and deformation mechanisms. But, as Butcher, Carroll, and Holt, (1974) noted, the elastic-perfectly plastic model is too simple to describe a variety of metal behaviors. Mechanisms such as strain hardening must be included to develop a model of general applicability. However, we will not consider such modifications. The readers are referred to the original papers.

An interesting aspect of the spherical pore collapse model is that its dynamic governing equations contain a characteristic time constant \( \tau \) given by (Carroll and Holt, 1972)

\[ \tau^2 = \frac{\rho_s a_0}{3Y(\alpha_0 - 1)^{2/3}} \]  

(48)

For aluminum with \( \rho_s = 2.71 \text{ g/cm}^3, a_0 = 20 \mu m, Y = 0.3 \text{ GPa}, \) and \( \alpha_0 = 1.3 \), \( \tau \) is approximately 0.05 \mu s.

It is interesting to compare this time constant with the time required to fill a characteristic void space by the motion of particle-free-surface excited by shock-
wave propagation.

\[ \tau_h = \frac{a_0}{2u_{fs}} \]

For the purpose of illustration approximate values of \( \tau_h \) are calculated for two shock pressures in Al.

\[ \tau_h = \begin{cases} 
0.02 \mu s; & p(\text{shock}) = 8.0 \text{GPa} \\
0.008 \mu s; & p(\text{shock}) = 22.0 \text{GPa} 
\end{cases} \]

It seems that a fairly strong shock is necessary before the hydrodynamic flow becomes the controlling mechanism of mass motion in void collapse. We shall return to those time constants when we examine the question of mass mixing under shock compression.

4.2.2 Continuum plasticity theory

Extension of the hydrodynamic models discussed above to include shear effects can be done in an expedient manner using the continuum plasticity theory. Although it is a phenomenological theory, it has proven to be a powerful technique for developing material models with sufficient generality to deal with a variety of types and loading conditions. It has been extensively used in the study not only of soils and other geological materials with a varying degree of porosity and compositions (DiMaggio and Sandler, 1971; Nelson et al., 1971; Drucker et al., 1957), but also die-compaction of metal and ceramic powders (Strijbos et al., 1979; Kuhn and Downey, 1971; Thomson, 1981; and Broese van Greunen, 1982). Extensive listings of the older literature are found in Cowin and Carroll (1976).

However, in spite of its generality, application of the CPT to shock wave propagation in powder materials is limited (Johnson and Green, 1976; Swegle, 1980; and Horie et al., 1985). Possible reasons for this lack of extensive use are

(a) Shear effects are small at very high pressures as we have seen in dense solids,

(b) Even at moderate pressure, shear effects may not be pronounced under the conditions of uniaxial strain,

(c) CPT requires a considerable amount of effort in determining materials constants,

(d) Predicted rate of volume changes with this type plasticity is much higher than those measured.

Nevertheless, CPT is an important tool to study shear effects in powder materials. As has been the case for the simulation of die compaction, the numerical simulation of shock recovery systems may ultimately require such an
approach. Therefore, we shall present a model that combines the strength of both the CPT and the $p-\alpha$ model (Swegel, 1980; Horie et al., 1985; Park, 1985). In their approach the volume change serves as an internal constraint of deformation (Kanatani, 1982) and the question of excessive volume changes does not arise. The model retains the usual theoretical framework of plasticity theory such as the associated flow rule. According to Kanatani this modification allows even the inclusion of flow due to frictional sliding within the framework of plasticity.

The mathematical formulation of the model has three basic elements: 1) Effects of pores on stress and strain, 2) elastic stress-strain relationships, and 3) plastic stress-strain relationships.

1) Effects of pores on stress and strain

In this section we shall use the following definition of $\alpha$ for notational simplicity.

$$\alpha = \frac{V_s}{V} \quad (49)$$

We assume that the overall stress components are related to those of the solid constituents by

$$p = \alpha \, p_s(V_s, E) = f_p(\alpha, V, E) \quad (50)$$

$$S_{ij} = \alpha \, S_{ij} \quad (51)$$

where $p_s$ is the equation of state of the solid constituent. $S_{ij}$ signify deviatoric stress component.

Equation (50) is an exact result for hydrodynamic loading, but in general it is a function of Poisson’s ratio.

Similarly, the elastic deviatoric strain increments $de^{e}_{ij}$ and $de^{e}_{ij}$ are partitioned in terms of the volume components,

$$\frac{de^{e}_{ij}}{de^{e}_{ij}} = \frac{dV_s}{V_s} = \frac{d\ln V_s}{d\ln V} \quad (52)$$

This equation is not appropriate when there is no volume change. In such cases, the following assumption may be introduced:

$$de^{e}_{ij} dS^{e}_{ij} = de^{e}_{ij} dS^{e}_{ij} \quad (53)$$
Physically, this means that in an elastic response all of the additional incremental work due to the shear is converted into the elastic stored energy of the solid. Such an assumption is certainly not unreasonable.

2) Elastic response

Homogeneous, isotropic Hooke’s law is assumed for elastic behavior. Using pressure and deviatoric stress increments, it is given by

\[ dp = K d\varepsilon_{kk}^e \]  \hspace{1cm} (54)

\[ ds_{ij} = 2\mu de_{ij}^e \]  \hspace{1cm} (55)

The \( p-\alpha \) relation may be determined using either the hollow sphere model ignoring Poisson’s effect, a phenomenological equation based on sound speed measurements, or models that include shear effects (Watt et al., 1976). Here, we follow Hermann’s empirical approach in which

\[ \left( \frac{d\alpha}{dP} \right)_{\text{elastic}} = \left( \frac{1}{h^2(\alpha)} - 1 \right) = \frac{1}{K_{s0}} \]  \hspace{1cm} (56)

where

\[ h(\alpha) = 1 + (1 - \alpha) \frac{C_0}{C_{s0}} \left( \frac{C_0 - 1}{1 - \alpha_0} \right) \]  \hspace{1cm} (57)

\( K_{s0} = \) solid bulk modulus at zero pressure,
\( C_{r0}, C_{s0} = \) sound velocity of the porous and material at zero pressure.

Equation (56) is derived from the sound speed formula

\[ C^2 = -V \left( \frac{\partial p}{\partial V} \right)_s \]  \hspace{1cm} (58)

and Eq. (50). That is, putting Eq. (50) into Eq. (58) yields
\[ C_i^2 = C_s^2 \left[ 1 + \frac{d\alpha}{dp} \left( K_{s0} - \frac{p}{\alpha} \right) \right]^{-1} \]

where \( c_i \) is the sound speed of the porous material. For small pressures \( (p/\alpha \ll K_{s0}) \),

\[ \frac{d\alpha}{dp} = \frac{1}{K_{s0}} \left[ \frac{C_i^2}{C_s^2} - 1 \right] \]

(59)

Comparing Eq. (56) with Eq. (59), it may be seen that in the former, \( h(\alpha) \) is chosen so that \( C_i \) varies linearly from \( C_{i0} \) to \( C_{i0} \) as \( \alpha \) varies from \( \alpha_0 \) to 1 (Swegle, 1980).

Elastic bulk and shear moduli of the porous material may be determined as follows. The bulk modulus results from the constraint that the pressures in Eqs. (50) and (56) are identical. That is,

\[ df_p = K_\alpha d\alpha^e = dp \]

Thus, using Eq. (54), one obtains

\[ K = -K_\alpha V \left( \frac{\partial f_p}{\partial V} \right) \left[ K_\alpha - \frac{\partial f_p}{\partial \alpha} \right] \]

(60)

Similarly the calculation of \( \mu \) is based on Eqs. (51), (52) and (55). It may be seen that

\[ \mu = \alpha \frac{d\epsilon^e_{ij}}{d\epsilon^v_{ij}} = \frac{dV^s}{dV} \mu_s = \alpha \mu_s \]

(61)

where \( \mu_s \) is the solid shear modulus.

3) Elastic-plastic response behavior

The mathematical development of stress-strain relation in plastic regime is very similar to that in Chapter 2. The difference is seen only in the yield function, the moduli of the porous material, and the length of algebra required to get to the final expressions. The major difference is the yield function, which will now be assumed as a function of three variables, \( J_2' \) (\( = 1/2(S_{ij}S_{ij}) \)), pressure, and \( \alpha \).

The four basic equations are:
Yield function

\[ g\left(J_1, \sqrt{J_2} \alpha \right) = 0 \]  \hspace{1cm} (62)

Strain increment in the plastic region

\[ d\varepsilon_{ij} = d\varepsilon_{ij}^e + de_{ij}^p \]

Associated flow rule

\[ de_{ij}^p = d\lambda \frac{\partial g}{\partial \sigma_{ij}} \]  \hspace{1cm} (63)

Increment of stress components

\[ dp = -Kd\varepsilon_{kk} = -K\left(d\varepsilon_{kk} - de_{kk}^p \right) \]  \hspace{1cm} (64)

\[ dS_{ij} = 2Gd\varepsilon_{ij}^e = 2G\left(d\varepsilon_{ij} - de_{ij}^p \right) \]  \hspace{1cm} (65)

We no longer introduce the assumption that \( de_{kk}^p = 0 \). With the flow rule, Eq. (63), we now find

\[ de_{kk}^p = d\lambda \frac{\partial g}{\partial \sigma_{11}} + d\lambda \frac{\partial g}{\partial \sigma_{22}} + d\lambda \frac{\partial g}{\partial \sigma_{33}} \]

\[ = 3d\lambda \frac{\partial g}{\partial J_1} \]

So, the deviatoric plastic strain increments are given by

\[ de_{ij}^p = d\varepsilon_{ij}^p - \frac{1}{3} de_{kk}^p \delta_{ij} \]

\[ = d\lambda \frac{\partial g}{\partial \sigma_{ij}} - d\lambda \frac{\partial g}{\partial J_1} \delta_{ij} \]
\[ \begin{align*}
  &= d\lambda \left( \frac{\partial g}{\partial \sqrt{J_2}} - \frac{\partial g}{\partial \sigma_{ij}} \frac{\partial \sigma_{ij}}{\partial J_1} \right) \\
  &= d\lambda \frac{S_{ij}}{2\sqrt{J_2}} \frac{\partial g}{\partial \sqrt{J_2}}
\end{align*} \]

Then, the stress relationships can be written as

\[ dp = -Kd\varepsilon_{kk} - 3Kd\lambda \frac{\partial g}{\partial J_1} \quad (66) \]

\[ dS_{ij} = 2Gd\varepsilon_{ij} - Gd\lambda \frac{S_{ij}}{\sqrt{J_2}} \frac{\partial g}{\partial \sqrt{J_2}} \quad (67) \]

As we have seen in Chapter 2, the derivation of \( d\lambda \) is based on the observation that the yield function, Eq. (62) must be satisfied for plastic loading. That is,

\[ dg = \frac{\partial g}{\partial J_1} dJ_1 + \frac{\partial g}{\partial \sqrt{J_2}} d\sqrt{J_2} + \frac{\partial g}{\partial \alpha} d\alpha = 0 \quad (68) \]

where

\[ dJ_1 = -3p = -3Kd\varepsilon_{kk} - 9Kd\lambda \frac{\partial g}{\partial J_1} \quad (69) \]

\[ d\sqrt{J_2} = \frac{(S_{ij}dS_{ij})}{2\sqrt{J_2}} = \frac{G(S_{ij}d\varepsilon_{ij})}{\sqrt{J_2}} - Gd\lambda \frac{\partial g}{\partial \sqrt{J_2}} \quad (70) \]

\( d\alpha \) is obtained from the \( p-\alpha \) equation.

\[ df_p = \frac{\partial f_p}{\partial \alpha} d\alpha + \frac{\partial f_p}{\partial V} dV \quad (71) \]
\[ d\alpha = \frac{\left( df_p - V \frac{\partial f_p}{\partial \alpha} d\varepsilon_{kk} \right)}{\frac{\partial f_p}{\partial \alpha}} \]

Additionally, we must satisfy the condition that the increment of the pressure \( df_p \) in Eq. (71) must be equal to the increment of the pressure in Eq. (66). Thus,

\[ d\alpha = \frac{\left( -K - V \frac{\partial f_p}{\partial \alpha} d\varepsilon_{kk} \right) + 3Kd\lambda \frac{\partial g}{\partial J_1} \}}{\frac{\partial f_p}{\partial \alpha}} \] (72)

Then, substituting Eqs. (69), (70) and (72) into Eq. (68), we find

\[ d\lambda = \frac{1}{H} \left[ 3K \frac{\partial g}{\partial J_1} d\varepsilon_{kk} + \frac{G S_j d\varepsilon_{ij}}{\sqrt{J_2}} \frac{\partial g}{\partial \sqrt{J_2}} + \left( -K - V \frac{\partial f_p}{\partial \alpha} \right) \frac{\partial g}{\partial \alpha} d\varepsilon_{kk} \right] \] (73)

where

\[ H = 9K \left( \frac{\partial g}{\partial J_1} \right)^2 + G \left( \frac{\partial g}{\partial \sqrt{J_2}} \right)^2 - 3K \left( \frac{\partial g}{\partial J_1} \right)^2 \] (74)

Finally, combining Eqs. (66) and (67), we obtain the stress strain relations (see Appendix at the end of this section).

\[ d\sigma_{ij} = -dp \delta_{ij} + dS_{ij} \]

\[ = \left( Kd\varepsilon_{kk} - 3Kd\lambda \frac{\partial g}{\partial J_1} \right) \delta_{ij} + 2Gd\varepsilon_{ij} - d\lambda \frac{G S_{ij}}{\sqrt{J_2}} \frac{\partial g}{\partial \sqrt{J_2}} \] (75)
\[
\begin{align*}
&= \left[ \left( K - \frac{2}{3} G \right) \delta_{ij} - C_i \delta_{ij} - C_2 S_{ij} \right] d e_{kk} - \left( C_3 \delta_{ij} + C_4 S_{ij} \right) \left( S_{ij} d e_{ij} \right) + 2 G d e_{ij} \\
\text{where}
\end{align*}
\]

\[
C_1 = \frac{1}{H} \left( \frac{3K}{\partial J_1} \frac{\partial g}{\partial J_1} - \left( K + V \frac{\partial f_p}{\partial \alpha} \frac{\partial g}{\partial \alpha} \right) \right) \tag{76}
\]

\[
C_2 = \frac{1}{H} \left( \frac{G}{\sqrt{J_2}} \frac{\partial g}{\partial J_2} - \left( K + V \frac{\partial f_p}{\partial \alpha} \frac{\partial g}{\partial \alpha} \right) \right) \tag{77}
\]

\[
C_3 = \frac{1}{H} \left( 3K \frac{\partial g}{\partial J_1} \left( \frac{G}{\sqrt{J_2}} \frac{\partial g}{\partial J_2} \right) \right) \tag{78}
\]

\[
C_4 = \frac{1}{H} \left( \frac{G}{\sqrt{J_2}} \frac{\partial g}{\partial J_2} \right)^2 \tag{79}
\]

It may be seen that when \( C_1, C_2, C_3, \) and \( C_4 \) are zero, the constitutive equation Eq. (75) becomes that of the elastic region. Table 4-1 shows the equation in a matrix form. For the case of unloading, elastic unloading may be assumed. If necessary, this could be modified to include yielding during unloading. The mathematical formulation is the same.

4.2.3 Application

Park (1985) considered two representative examples. The first was a reexamination of the 22% porous aluminum studied by Swegle (1980) who used data by Johnson and Greene (1976). The second example was Ottawa sand. We shall describe the first example in this section.

Park employed the same solid equation of state and the yield function proposed by Swegle. They are
Table 4-1. Stress-strain relationship of the CPT model.

<table>
<thead>
<tr>
<th>$\sigma_{11}$</th>
<th>$K + \frac{4}{3}G$</th>
<th>$-(C_3 + C_4 S_{11}) S_{12}$</th>
<th>$-(C_3 + C_4 S_{11}) S_{13}$</th>
<th>$K - \frac{2}{3}G$</th>
<th>$-(C_1 + C_2 S_{11} + (C_3 + C_4 S_{11}) S_{22})$</th>
<th>$-(C_3 + C_4 S_{11}) S_{23}$</th>
<th>$K - \frac{2}{3}G$</th>
<th>$-(C_1 + C_2 S_{11} + (C_3 + C_4 S_{11}) S_{23})$</th>
<th>$d\varepsilon_{11}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_{12}$</td>
<td>$-(C_2 + C_4 S_{11}) S_{12}$</td>
<td>$G - C_4 S_{12}^2$</td>
<td>$-C_4 S_{12} S_{13}$</td>
<td>$-(C_2 + C_4 S_{12}) S_{12}$</td>
<td>$-C_4 S_{12} S_{23}$</td>
<td>$-(C_2 + C_4 S_{12}) S_{23}$</td>
<td>$-(C_2 + C_4 S_{12}) S_{23}$</td>
<td>$2d\varepsilon_{12}$</td>
<td></td>
</tr>
<tr>
<td>$\sigma_{13}$</td>
<td>$-(C_2 + C_4 S_{11}) S_{13}$</td>
<td>$-C_4 S_{12} S_{13}$</td>
<td>$G - C_4 S_{13}^2$</td>
<td>$-(C_2 + C_4 S_{13}) S_{13}$</td>
<td>$-C_4 S_{13} S_{23}$</td>
<td>$-(C_2 + C_4 S_{13}) S_{23}$</td>
<td>$-(C_2 + C_4 S_{13}) S_{23}$</td>
<td>$2d\varepsilon_{13}$</td>
<td></td>
</tr>
<tr>
<td>$\sigma_{22}$</td>
<td>$K - \frac{2}{3}G$</td>
<td>$-(C_1 + C_4 S_{22}) S_{22}$</td>
<td>$-(C_1 + C_4 S_{22}) S_{23}$</td>
<td>$K + \frac{4}{3}G$</td>
<td>$-(C_1 + (C_2 + C_3) S_{22}) + C_4 S_{22}^2$</td>
<td>$-(C_1 + C_4 S_{22}) S_{23}$</td>
<td>$K - \frac{2}{3}G$</td>
<td>$-(C_1 + (C_2 + C_3) S_{22} + (C_3 + C_4 S_{22}) S_{23})$</td>
<td>$d\varepsilon_{22}$</td>
</tr>
<tr>
<td>$\sigma_{23}$</td>
<td>$-(C_2 + C_4 S_{23}) S_{23}$</td>
<td>$-C_4 S_{23} S_{23}$</td>
<td>$-C_4 S_{23} S_{23}$</td>
<td>$G - C_4 S_{23}^2$</td>
<td>$-(C_2 + C_4 S_{23}) S_{23}$</td>
<td>$-C_4 S_{23} S_{23}$</td>
<td>$-(C_2 + C_4 S_{23}) S_{23}$</td>
<td>$2d\varepsilon_{23}$</td>
<td></td>
</tr>
<tr>
<td>$\sigma_{33}$</td>
<td>$K - \frac{2}{3}G$</td>
<td>$-(C_1 + C_4 S_{33}) S_{32}$</td>
<td>$-(C_1 + C_4 S_{33}) S_{33}$</td>
<td>$K - \frac{2}{3}G$</td>
<td>$-(C_1 + C_4 S_{32}) S_{33}$</td>
<td>$-(C_1 + C_4 S_{33}) S_{33}$</td>
<td>$K + \frac{4}{3}G$</td>
<td>$-(C_1 + (C_2 + C_3) S_{33}) + C_4 S_{33}^2$</td>
<td>$d\varepsilon_{33}$</td>
</tr>
</tbody>
</table>

\* $d\sigma_{12} = d\sigma_{11}, d\sigma_{13} = d\sigma_{11}, d\sigma_{23} = d\sigma_{12}$
\[ p_s = A \left( \frac{V_{s0}}{V_s} - 1 \right) + B \left( \frac{V_{s0}}{V_s} - 1 \right)^2 + C \left( \frac{V_{s0}}{V_s} - 1 \right)^3 \]  
(80)

\[ \left( \frac{p}{p_1(\alpha)} \right)^2 + \left( \frac{\sqrt{3J_2}}{Y_1(\alpha)} \right)^2 + 1 = 0 \]  
(81)

where \( P_1(\alpha) \) and \( Y_1(\alpha) \) are expressed by cubic spline functions,

\[ f_i = A_i + B_i(\alpha - \alpha_i) + C_i(\alpha - \alpha_i)^2 + D_i(\alpha - \alpha_i)^3, \quad \alpha_i < \alpha < \alpha_{i+1} \]

However, Park correlated \( Y_1 \) with \( P_1 \) to reduce the required number of material constants. The result is

\[ Y_1(\alpha) = Q(1 - \alpha)^m p_1(\alpha) \]  
(82)

where \( Q \) and \( m \) are constant.

Table 4-2 summarizes the material constants used by Park (1985). They are obviously identical to those of Swegle except those associated with \( Y_1(\alpha) \).

Park tested the new constants using the static compression data of Johnson and Green (1976). Figure 4-14 shows a comparative result of model calculations and measurements. In the former, the cubic \( P_1(\alpha) \) function is fitted to the hydrostatic data.

Predicted uniaxial strain behavior is in agreement with the experiment to about 0.1 GPa, but deviates from it because of continuing shear-enhanced pore compaction. That is, the calculation did not show the “cross-over” phenomenon of uniaxial strain data above 0.25 GPa.

Swegle’s material constants were chosen so that the model duplicates the cross-over phenomenon in the \( p-V' \) plane. But, Park pointed out that such a selection produces peculiar behavior in the stress difference \( (\sigma_1 - \sigma_3) \) as shown in Fig. 4-15. Swegle thought that the cross-over of the curves was caused by strain hardening, but it is likely (Johnson, 1983) that the experiment is suspect.

Recently, there have been studies of instability in granular flow that is associated with the type of yield functions used in this section (Pitman and Schaeffer, 1987). They point out an interesting possibility of wave structure behind the shock front in powder mixture, but they are beyond the scope of this book.
Table 4-2. Material constants of 22% porous aluminum.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_0$</td>
<td>0.78</td>
</tr>
<tr>
<td>$P_0$</td>
<td>2.7 g/cm³</td>
</tr>
<tr>
<td>$G_0$</td>
<td>27.4 GPa</td>
</tr>
<tr>
<td>$K_0$</td>
<td>78.2 GPa</td>
</tr>
<tr>
<td>$c_0/c_0^0$</td>
<td>0.528</td>
</tr>
<tr>
<td>$A$</td>
<td>78.2</td>
</tr>
<tr>
<td>$B$</td>
<td>172</td>
</tr>
<tr>
<td>$C$</td>
<td>40</td>
</tr>
<tr>
<td>$D$</td>
<td>0</td>
</tr>
</tbody>
</table>

The coefficients of cubic spline functions for $p(\alpha)$ and $Y(\alpha)$ are

for $p(\alpha)$

<table>
<thead>
<tr>
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<th>Value</th>
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<tr>
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<td>0.77823</td>
</tr>
<tr>
<td>$\alpha_2$</td>
<td>0.96158</td>
</tr>
<tr>
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</tr>
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<tr>
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<tr>
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</tr>
<tr>
<td>$D_2$</td>
<td>8441.51</td>
</tr>
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</table>

for $Y(\alpha)$

<table>
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</thead>
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<tr>
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<tr>
<td>$m_1$</td>
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</tr>
<tr>
<td>$m_2$</td>
<td>0.21</td>
</tr>
</tbody>
</table>

$P < 0.1$ GPa

$P > 0.1$ GPa

Fig. 4-14. Model calculations and experimental data of the pressure-volume response of 22% porous aluminum under hydrostatic and uniaxial loadings.
Fig. 4-15. A comparison of two model calculations of the stress difference as a function of pressure with experimental data of Johnson and Green.

Derivation of the Elasto-Plastic Stress and Strain Relation

The stress increment is decomposed into two parts.

\[ d\sigma_{ij} = -dP\delta_{ij} + dS_{ij} \]

Upon substituting Eq. (64) and (65) into \(dP\) and \(dS_{ij}\) above, we can write the stress increment \(d\sigma_{ij}\) as follows:

\[
d\sigma_{ij} = \left( Kd\varepsilon_{kk} - 3Kd\lambda \frac{\partial g}{\partial J_1} \right) \delta_{ij} + 2Gd\varepsilon_{ij} - d\lambda \frac{GS_{ij}}{\sqrt{J_2'}} \frac{\partial g}{\partial \sqrt{J_2'}}
\]

\[
= \left( K - \frac{2}{3} G \right) d\varepsilon_{kk} \delta_{ij} + 2Gd\varepsilon_{ij} - d\lambda \left( 3K \frac{\partial g}{\partial J_1} \delta_{ij} + \frac{GS_{ij}}{\sqrt{J_2'}} \frac{\partial g}{\partial \sqrt{J_2'}} \right)
\]

\(d\lambda\) is given by Eq. (73),
\[ d\lambda = \frac{1}{H} \left[ 3K \frac{\partial g}{\partial J_1} d\varepsilon_{kk} + \frac{G}{\sqrt{J'_2}} \frac{\partial g}{\partial \sqrt{J'_2}} \left( S_y d\varepsilon_{ij} \right) - \left( K + V \frac{\partial f_p}{\partial V} \right) \frac{\partial g}{\partial \alpha} d\varepsilon_{kk} \right] \]

\[ = \frac{1}{H} \left[ C_K d\varepsilon_{kk} + \frac{G}{\sqrt{J'_2}} \frac{\partial g}{\partial \sqrt{J'_2}} \left( S_y d\varepsilon_{ij} \right) \right] \]

where

\[ C_K = 3K \frac{\partial g}{\partial J_1} \left( K + V \frac{\partial f_p}{\partial V} \right) \frac{\partial g}{\partial \alpha} \]

\[ H = 9K \left( \frac{\partial g}{\partial J_1} \right)^2 + G \left( \frac{\partial g}{\partial \sqrt{J'_2}} \right)^2 - 3K \left( \frac{\partial g}{\partial J_1} \right)^2 \]

Hence,

\[ d\sigma_{ij} = \left( K - \frac{2}{3} G \right) d\varepsilon_{kk} \delta_{ij} + 2Gd\varepsilon_{ij} \]

\[ - \frac{1}{H} \left[ C_K d\varepsilon_{kk} + \frac{G}{\sqrt{J'_2}} \frac{\partial g}{\partial \sqrt{J'_2}} \left( S_y d\varepsilon_{ij} \right) \right] \left( 3K \frac{\partial g}{\partial J_1} \delta_{ij} + \frac{GS_{ij}}{\sqrt{J'_2}} \frac{\partial g}{\partial \sqrt{J'_2}} \right) \]

\[ d\sigma_{ij} = \left[ \left( K - \frac{2}{3} G \right) \delta_{ij} - C_1 \delta_{ij} - C_2 S_{ij} \right] d\varepsilon_{kk} - \left[ C_3 \delta_{ij} + C_4 S_{ij} \right] \left( S_y d\varepsilon_{ij} \right) + 2Gd\varepsilon_{ij} \]
where

\[ C_1 = \frac{C_k}{H} 3K \left( \frac{\partial g}{\partial J_1} \right) \]

\[ C_2 = \frac{C_k}{H} \frac{G}{\sqrt{J_2'}} \left( \frac{\partial g}{\partial \sqrt{J_2'}} \right) \]

\[ C_3 = \frac{1}{H} \left( 3K \frac{\partial g}{\partial J_1} \right) \left( \frac{G}{\sqrt{J_2'}} \frac{\partial g}{\partial \sqrt{J_2'}} \right) \]

\[ C_3 = \frac{1}{H} \left( \frac{G}{\sqrt{J_2'}} \frac{\partial g}{\partial \sqrt{J_2'}} \right)^2 \]

Note:

\[ \left( S_{ij} d e_{ij} \right) = S_{11} d e_{11} + S_{12} d e_{12} + S_{13} d e_{13} + S_{21} d e_{21} + \ldots + S_{33} d e_{33} \]

4.3 Particle Bonding and Heterogeneous Processes

If voids exist in a continuous matrix, then the question of particle bonding does not arise. When the voids disappear, a dense solid emerges automatically. The Carroll-Holt model is of this type. But in the case of powders the disappearance of voids is not synonymous with bonding or welding of particles. The model based on particles-in-contact has features that are important in the consideration of particles bonding, but it does not address the question. It seems that an understanding of bonding processes requires new concepts.

According to Rumpf (1962), bonding of particles can be attributed to a variety of mechanisms such as mechanical interlocking, electrostatic forces, and interfacial forces. But, in this section the term “bonding” is used to mean bonding that involves the transfer of atoms across contact interfaces and the reconstruction of their bonds. In this context, there are two important requirements for the process of bonding to take place:

(a) Transport of atoms, and

(b) Reduction of surface energies resulting from the formation of interfacial bonds.

The first process is typically controlled by temperature, but defects such as
dislocations will substantially augment it. The second requirement is sensitive to the nature of chemical bonding of atoms. Therefore, the joining of covalently bonded materials such as diamond and SiC is difficult because of their special requirements in atomic spacing and bond angles. By contrast the rearrangement of metallic bonds is not so restricted as covalent bonds. The conditions on ionic materials lie between metals and covalent materials.

It is known with metals, that if their surfaces are clean and free of foreign atoms, then light contact is sufficient to establish bonds even at room temperatures (Czychos, 1972). This phenomenon may also happen between a metal and an ionic material (e.g., Al/Al₂O₃, Akaike and Funakubo, 1980). But, with covalent materials high temperatures are required to disrupt strong atomic bonds and initiate mass diffusion.

Since powders are normally covered with thin layers of oxides and other contaminants, the formation of bonds between particles requires high temperatures or mechanical removal of the contaminant layers by fracture or plastic deformation or both. Such a requirement is dramatically illustrated in Fig. 4-16 where the development of bond strength in pure shear is plotted as a function of the surface expansion for several metal combinations (Bay, 1979). The figure clearly shows that bonding is not created until a large surface expansion is reached. This means that the type of plastic deformation used in the model calculations of pore collapse in the previous section is not likely to produce strong bonding of particles. More intensely heterogeneous, localized deformations seem to be required to explain bonding under shock compression.

![Graph showing the evolution of interfacial bond strength as a function of surface expansion due to rolling (after Bay, 1979).](image-url)
Morris (1983) proposed four possible mechanisms of preferential surface deformation illustrated in Fig. 4-17. They are (1) jetting, (2) jet trapping, (3) frictional sliding, and (4) dominant features observed in shock compacted metallic powders: localized intense material flow often giving the appearance of (a) pinched or squeezed flow between particles and (b) interlocking waves reminiscent of explosive welding. This flow will lead to melting at the appropriate conditions of deformation and frictional rubbing. However, these mechanisms have not been related to bonding in a quantitative form.

![Possible bonding mechanisms of powders during shock compression: (a) explosive bonding, (b) jet trapping, (c) frictional sliding, and (d) point deformation (after Morris, 1983).](image)

Schwartz et al. (1984) have developed a model in which surface melting is hypothesized a priori and its amount is calculated based on the ratio of the energy required to melt a unit mass and the total dissipated energy behind the shock front. Then, the window of processing parameters is discussed in terms of the minimum melt fraction and the minimum duration of the shock state to assure resolidification of the melt.

There are several models that have attempted to account for thermal histories of heterogeneous energy depositon (e.g., Raybould, 1981; Gourdin, 1984) through the surface of a spherical particle. But, none was related to the question of consolidation. Kondo et al. (1985) also considered a depositions of dissipated energy in a thin surface region called “skin” and used it to evaluate the shock processing of ceramic powders. The problem with any of these models is that the predictions are sensitive to a priori assumptions of the volume over which energy is deposited. Hence predicted numerical values of temperature can easily vary an order of magnitude. Indeed in the limit of vanishingly small volumes, any small increment of energy will lead to infinitely large increases in temperature.
Also, none of these models involve actual physical mechanisms of energy dissipation. Short of numerical simulations such as those of Williamson and Berry (1986), the modeling of heterogenous processes in real powders, including microstructural changes, may be close to impossibility. Most models are focused just on the thermal aspects of an assumed heterogeneous depositon of energy. Nevertheless, the model proposed by Schwartz et al. does provide certain bounds on process parameters with the distinct advantage of being analytical. Probably, it is the most practical model developed so far for the shock consolidation of powders. The strength of this model is the establishment of a processing map in terms of input energy and shock duration.

The Schwartz et al. model identifies two important stages of the consolidation process. The first stage is densification and partial melting of particles that are assumed to take place within the shock front. The rise time \( t_r \) is approximated by \( d/U \) where \( d \) is the average particle diameter. The second is solidification of the melted regions. The characteristic time \( t_s \) is calculated based on Newtonian cooling of a melted slab of thickness \( h \) without superheating of the melt in contact with a semi-infinite solid at \( T \). The thickness is related to the particle diameter by \( h = Ld \) in which \( L \) is the mass fraction melted. The result is

\[
t_s = \frac{\pi D_m}{16} \left[ \frac{LdH_m P}{K_m \left( T_m - T' \right)} \right]^2
\]

(83)

where \( D_m = \) the thermal diffusivity = \( K_m / \rho C_{pm} \), \( K_m \) is the thermal conductivity, "\( m \)" refers to melting temperature, and \( T' \equiv \) room temperature.

By contrast the relaxation time to a homogeneous bulk temperature \( t_h \) is much longer and given by

\[
t_h = \frac{d^2}{64 D_m}
\]

The calculation of the key parameter \( L \) introduces two additional assumptions. The first is that the dissipated work during powder compaction is given by

\[
\Delta E_T = \frac{P(V_0 - V_{s0})}{2} = \frac{PV_0(m-1)}{2}
\]

(84)

where \( P \) is the shock pressure, \( m = V_0/V_{s0} \).

The second is that the work spent in heating and melting the mass fraction is done adiabatically and approximated by Eq. (83). Then, it may be seen that the
upper bound of $L$ is

$$L_u = \frac{\Delta E_T}{\left[ \overline{C_p}(T_m - T_0) + H_m \right]}$$  

(85)

where $\overline{C_p}$ is the average $C_p$ in the region $(T_0 - T_m)$ and $H_m$ the heat of fusion. This is the upper bound for $L$. The lower bound according to Vreeland et al. (1986) is the melt fraction calculated under thermal equilibrium conditions when the input shock energy exceeds that required to form melt, and is given by

$$L_l = \frac{\Delta E_T - \overline{C_p}(T_m - T_0)}{H_m}$$

The experimental data for Markomet 1064 alloy are found between the two bounds (Vreeland et al., 1986).

Particles are assumed to be surrounded uniformly by melt after the passage of a shock. But its core regions remain cool. Also, it is thought that the melted regions must solidify and cool to below $T_m$ while the sample is still in the shock state. Otherwise the sample is thought to disintegrate by tension that may result in the subsequent unloading phase. Thus,

$$t_d \ (\text{shock duration}) > t_s + t_c$$  

(86)

where $t_c$ is the cooling time. In the original analysis $t_c$ is set to be zero because of difficulty in estimating the cooling time to acquire strength.

Now, putting Eqs. (83) and (85) in Eq. (86) yields

$$\tau_d^{1/2} \geq \varepsilon \left[ 2\sqrt{\pi} \left( \frac{\overline{C_p}}{C_{pm}} \right) \frac{H_m}{\left[ \overline{C_p}(T_m - T_0) + H_m \right]} \right]$$  

(87)

where $\tau_d$ and $\varepsilon$ are the normalized time and energy defined by

$$\tau_d = \frac{t_d}{\left( \frac{d^2}{64D_m} \right)}$$
\[ \varepsilon = \frac{pV_0(m - 1)}{2C_p(T_m - T_0)} \]

Note that \( \varepsilon \) does not contain the heat of fusion.

The upper limit of \( \varepsilon \) located at, and corresponds to, total melting of the powder. At this limit the thermal relaxation of the particles is controlled by ambient bulk conditions. Hence, its characteristic time is far greater than \( t_r \).

The lower limit is determined empirically. For iron based powders, the limit is found to be

\[ \varepsilon > 1.7 \varepsilon_b, \quad \varepsilon_b = 0.18 \]  \( (88) \)

The resulting processing map based on the three bounding conditions is illustrated in Fig. 4-18.

Recently, Ferreira (1989) attempted to determine the minimum energy

![Fig. 4-18. Dynamic consolidation map for an iron-base powder by shock compression. The solid and half-solid symbols denote compacts with UTS larger and smaller that 0.8 GPa, respectively. The open square denotes a compact with microcracks (after Schwartz et al., 1984).](image-url)
requirement based on the several sources of energy dissipation:

\[ \Delta E = \text{void collapse} + \text{melting} + \text{deformation} / \text{hardening} + \text{kinetic energy}. \]

No mechanistic bases are proposed for the minimum thickness layer needed for consolidation. It would be interesting and helpful if particle bonding were modeled using the particles-in-contact viewpoint. Particularly important is an understanding of the evolution of bonding strength in terms of process parameters and their influence on interfacial conditions.

Schwartz et al. (1984) offers an interesting conjecture based on the condition, \( t_r \ll t_h \), that the minimum particle size for shock consolidation is given by

\[ d \geq 64 D_m / U \]  

(89)

For \( D_m = 5.16 \times 10^{-6} \) m²/s (iron) and \( U = 2 \) km/s. Eq. (89) requires \( d \geq 0.17 \) μm. Recently, Kondo and Sawai (1990) obtained diamond compacts that appear to counter the above conjecture.

4.4 Mass Mixing

The question of mass transport is one of the central issues in the study of shock-induced chemical reactions in condensed matter. Modern fabrication techniques may be used to prepare premixed samples at atomic level, but reactants in most experiments with mixed powders are often separated from each other over the distance of tens of micrometers. In addition, products in condensed-phase often become barriers to mass transfer as well as to the propagation of reactions.

A rule of thumb for estimating the distance of atomic diffusion is

\[ (Dt)^{1/2} \]  

(90)

where \( D \) is the diffusion coefficient and \( t \) time. Table 4-3 shows representative values of \( D \) for elemental metals. Figure 4-19 shows melting point diffusivity for classes of crystalline solids. Choosing the values of \( 10^{-8} \) cm²/s and \( 10^{-6} \) s for \( D \) and \( t \) respectively, one obtains the diffusion distance of \( 10^{-7} \) cm during the characteristic time of shock compression. So, it is suspected that mass diffusion is negligible during the time of shock compression and that observed reactions in recovered samples occurred after the passage of the shock wave. An attempt to measure mass diffusion directly in real time using a combination of copper and a transparent dielectric (LiF or Plexiglass) was not successful (Yakusheva et al., 1970).

However, there have been reports of unusual mass transport under shock loadings. For instance, Zemsky et al. (1978) investigated the mass transfer of
Table 4-3. Self-diffusion in elemental metals.

<table>
<thead>
<tr>
<th>Element</th>
<th>Crystal Structure</th>
<th>$T_m$ (K)</th>
<th>$\Delta T$ (kcal)</th>
<th>$D_\infty$ (cm$^2$/sec)</th>
<th>$D(T_m/2)$</th>
<th>$D(T_m)$</th>
<th>$D(300K)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>bcc</td>
<td>337</td>
<td>9.36</td>
<td>0.16</td>
<td>$1.1 \times 10^{-13}$</td>
<td>$1.4 \times 10^{-7}$</td>
<td>$2.4 \times 10^{-8}$</td>
</tr>
<tr>
<td>Na</td>
<td>bcc</td>
<td>371</td>
<td>11.5</td>
<td>0.72</td>
<td>$2.0 \times 10^{-14}$</td>
<td>$1.2 \times 10^{-7}$</td>
<td>$3.0 \times 10^{-9}$</td>
</tr>
<tr>
<td>Cd$^a$</td>
<td>hcp</td>
<td>594</td>
<td>18.2</td>
<td>0.12</td>
<td>$4.8 \times 10^{-15}$</td>
<td>$2.4 \times 10^{-8}$</td>
<td>$6.5 \times 10^{-15}$</td>
</tr>
<tr>
<td>Cd$^b$</td>
<td>hcp</td>
<td>594</td>
<td>19.1</td>
<td>0.18</td>
<td>$1.6 \times 10^{-15}$</td>
<td>$1.7 \times 10^{-8}$</td>
<td>$2.2 \times 10^{-15}$</td>
</tr>
<tr>
<td>Al</td>
<td>fcc</td>
<td>933</td>
<td>34.0</td>
<td>1.71</td>
<td>$2.0 \times 10^{-16}$</td>
<td>$1.8 \times 10^{-8}$</td>
<td>$2.8 \times 10^{-25}$</td>
</tr>
<tr>
<td>Cu</td>
<td>fcc</td>
<td>1110</td>
<td>50.4</td>
<td>0.1</td>
<td>$1.4 \times 10^{-21}$</td>
<td>$1.2 \times 10^{-11}$</td>
<td>$1.8 \times 10^{-38}$</td>
</tr>
<tr>
<td>Ge</td>
<td>dc</td>
<td>1210</td>
<td>68.5</td>
<td>7.8</td>
<td>$1.4 \times 10^{-24}$</td>
<td>$3.3 \times 10^{-12}$</td>
<td>$9.1 \times 10^{-50}$</td>
</tr>
<tr>
<td>Ag</td>
<td>fcc</td>
<td>1234</td>
<td>45.2</td>
<td>0.67</td>
<td>$6.4 \times 10^{-17}$</td>
<td>$6.5 \times 10^{-9}$</td>
<td>$7.6 \times 10^{-34}$</td>
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<tr>
<td>Au</td>
<td>fcc</td>
<td>1336</td>
<td>42.1</td>
<td>0.09</td>
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<td>$1.8 \times 10^{-32}$</td>
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<td>Si</td>
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<td>115.8</td>
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<td>$1.3 \times 10^{-12}$</td>
<td>$5.7 \times 10^{-82}$</td>
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<tr>
<td>Ni</td>
<td>fcc</td>
<td>1726</td>
<td>67.2</td>
<td>1.23</td>
<td>$1.1 \times 10^{-17}$</td>
<td>$3.8 \times 10^{-9}$</td>
<td>$1.3 \times 10^{-49}$</td>
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<tr>
<td>Fe$^c$</td>
<td>fcc</td>
<td>68.9</td>
<td>0.49</td>
<td>$1.9 \times 10^{-17}$</td>
<td>$(3.0 \times 10^{-9})$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe$^d$</td>
<td>bcc</td>
<td>1809</td>
<td>57.4</td>
<td>1.39</td>
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<td>$1.6 \times 10^{-7}$</td>
<td>$2.0 \times 10^{-42}$</td>
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<tr>
<td>Pt</td>
<td>fcc</td>
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<td>68.1</td>
<td>0.33</td>
<td>$1.6 \times 10^{-17}$</td>
<td>$2.3 \times 10^{-9}$</td>
<td>$7.6 \times 10^{-51}$</td>
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<tr>
<td>Mo</td>
<td>bcc</td>
<td>2883</td>
<td>104.5</td>
<td>0.13</td>
<td>$1.8 \times 10^{-17}$</td>
<td>$1.5 \times 10^{-9}$</td>
<td>$8.7 \times 10^{-78}$</td>
</tr>
</tbody>
</table>

$^a$ || to hcp c-axis
$^b$ || to hcp c-axis
$^c$ fcc Fe
$^d$ bcc Fe


Fig. 4-19. Melting diffusivities for classes of crystalline solids. Numbers to the right of the boxes give the number of component examples (after Brown and Ashby, 1980).
carbon in iron using a radioscope technique at a pressure of the order of several hundreds kilobars. Their finding is that the observed penetration of $C^{14}$ from the contact interfacial into the specimen requires the "diffusion" coefficient of about $10^{-2}$ cm/s at $t = 3 \times 10^{-5}$ s. This value is several orders of magnitude greater than the values typically known for carbon in iron (see Table 4-4). They suggested the following three reasons to account for the high penetration rate: (a) acceleration of diffusion due to large stress gradient in the shock front, (b) influence of shock-generated defects, and (c) the possibility of "mechanical diffusion" proposed by Ruoff (1967).

The report of very large diffusion constants is not limited to shock loading. There is a similar report (Gostomel'skii and Roitburd, 1986) of an anomalously high mass transfer near an interface between dissimilar materials (carbon iron and nickel/copper) subjected to plastic deformation at low rates of loadings ($\dot{\varepsilon} \approx 90$ s$^{-1}$). Their estimate of the effective diffusion coefficient is about $10^{-3}$ cm$^2$/s. The mechanism is attributed to dislocation assisted diffusion.

Further, it has been known for some time that combined static loading of pressure and shear produces explosive reactions in thin layers of materials (Bridgman, 1937; Zorin et al., 1985; Burov et al., 1986). It is noteworthy that the tests by the latter two authors were conducted with powders. They noted that the process of mixing at an atomic level did not practically depend on pressure, temperature, and the rate of shear, and that the mechanism of the intensive mass transfer is due to a large number of defects produced under the combined loading.

Recently Whittenberger (1990) examined the enhancement of diffusion processes in high-energy ball milling by introduction of large numbers of dislocations and a high nonequilibrium concentration of vacancies.

Following Shevmon, he assumes that the enhancement of diffusion coefficient associated with dislocations is given by

$$D_c = f_c D_e$$

(91)

$$f_c = \frac{n \Gamma}{N}$$

(92)

where $f_c$ is the fraction of atoms associated with dislocation core, and $D_c$ the diffusion coefficient along the dislocation core, $n$ the number of atoms per unit length in the dislocation core, $\Gamma$ the dislocation density, and $N$ the atoms per unit area per unit length of dislocation. Then, he selects the following as representative numbers: $n = 5$ atoms/unit length in the core, $\Gamma = 10^{16}$ lines/m$^2$ and $N = 1 \times 10^{19}$/m$^2$/unit length of dislocation. With these numbers, $f_c$ equals 0.005. Thus,

$$D_e = 0.005 D_c$$

(93)
Table 4-4. Data pertaining to self-diffusion and C-diffusion in α-Fe (Courtesy of H. Conrad, NCSU).

<table>
<thead>
<tr>
<th></th>
<th>Bulk Diffusion</th>
<th>Grain Boundary Diffusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D_n ) (cm(^2)/s)</td>
<td>( \mathcal{Q}_f ) (eV)</td>
<td>( \mathcal{Q}_m ) (eV)</td>
</tr>
<tr>
<td>0.5(^{\text{(1)}})</td>
<td>1.3±0.4(^{\text{(2)}})</td>
<td>0.68(^{\text{(3)}})</td>
</tr>
<tr>
<td>118(^{\text{(4)}})</td>
<td>1.24±0.14(^{\text{(2)}})</td>
<td>2.92(^{\text{(4)}})</td>
</tr>
<tr>
<td>18(^{\text{(4)}})</td>
<td></td>
<td>2.78(^{\text{(4)}})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( D_0 ) (cm(^2)/s)</th>
<th>( \mathcal{Q}_C ) (eV)</th>
<th>( \mathcal{Q}_C^{\text{e-r}} ) (eV)</th>
<th>( \mathcal{Q}_S^{\text{e-r}} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.008(^{\text{(8)}})</td>
<td>0.086(^{\text{(8)}})</td>
<td>0.43(^{\text{(2)}})</td>
<td>0.41(^{\text{(2)}})</td>
</tr>
<tr>
<td>0.004(^{\text{(9)}})</td>
<td>0.83(^{\text{(9)}})</td>
<td>0.41(^{\text{(10)}})</td>
<td>0.41(^{\text{(11)}})</td>
</tr>
<tr>
<td>0.026(^{\text{(10)}})</td>
<td>0.89(^{\text{(10)}})</td>
<td></td>
<td>0.41(^{\text{(3)}})</td>
</tr>
<tr>
<td>0.86(^{\text{(11)}})</td>
<td></td>
<td></td>
<td>0.40(^{\text{(12)}})</td>
</tr>
<tr>
<td>4.0(^{\text{(12)}})</td>
<td>0.833(^{\text{(12)}})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.02(^{\text{(4,13)}})</td>
<td>0.87(^{\text{(6,13)}})</td>
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</table>

Numbers in parenthesis are references given below.

- \( D_0 \), \( \mathcal{Q}_f \), \( \mathcal{Q}_m \) and \( \mathcal{Q}_D \) are the pre-exponential and the energies respectively for vacancy formation, vacancy migration and self-diffusion in α-Fe.
- \( D_0^C \), \( \mathcal{Q}_C \), \( \mathcal{Q}_C^{\text{e-r}} \) and \( \mathcal{Q}_S^{\text{e-r}} \) are the pre-exponential and the energies respectively for single C atom diffusion, C-vacancy complex migration and C-vacancy binding.

\( D_c \) is assumed to be similar to atomic mobility in grain boundaries and given by

\[
D_c = D_0 \exp \left( \frac{-Q}{RT} \right)
\]

\[
= 10^{-5} \exp \left( -9.1 \frac{T_m}{T} \right)
\] (94)

where it is invoked that the pre-exponentials for volume and grain boundary diffusion are similar \( (D_0 = 10^{-5} \text{ m}^2/\text{s}) \) and that the activation energy for grain/ boundary diffusion is about half that for volume diffusion \( (Q = 151 \ T_m/2 \text{ kJ/mol}) \). Then, putting Eq. (94) into Eq. (93) yields the diffusivity enhancement due to dislocations.

Reaction time to make a binary product from pure elements is estimated to be

\[
t \approx \frac{(d/\varepsilon)^2}{D_c}
\]

where \( \varepsilon \) is a geometric factor \( (= 8) \) for a one dimensional, infinite solid diffusion couple. Then, with Eq. (93), this becomes

\[
t = \frac{3.125 \times 10^5 d^2}{\exp(-9.1 \ T_m/T)}
\] (95)

At \( T = T_m \) and \( d = 1 \ \mu\text{m} \) a typical reaction time is of the order of milliseconds, which are several orders of magnitude longer than the duration of shock compression.

There is, however, accumulating evidence that suggest chemical reactions do take place during shock wave compression. A great number and variety of defects generated under shock compression do augment chemical reactions, but defect-controlled mechanisms may be too slow to explain such reactions. There appear to be some other mechanism operating at a mesoscopic level \( (\sim \mu\text{m}) \) that increase mass mixing drastically by reducing the effective particle size from \( \mu\text{m} \) to sub-\( \mu\text{m} \).

Our current speculation is that they are related to some sort of localized instability phenomena. Representative candidates are:

(a) inhomogeneous plastic flows such as adiabatic shear and slips,
(b) interface instabilities,
(c) hydrodynamic instabilities such as turbulence. Since shock loading is known to reduce crystallite size down to several hundreds of angstroms (e.g., Morosin, 1987), the instabilities, if extensive enough, can lead to mixing of “crystallite grains” at sub-μm level.

Figure 4-20 shows an indication of such possibilities. The figure shows metallographs of Ni-coated aluminum powder consolidated at four impact-velocities on a gas gun. The starting powder has 80 w/o Ni and the nominal particle size of 53 to 88 μm. The range of impact velocity was 500–800 m/s. There are two noteworthy features in these metallographs. The first is the homogenization of Ni/Al indicated by the reduction of pure aluminum, caused, no doubt, by shock activation and heating. The second is the sudden loss of regularity in packing arrangement at 800 m/s that appears to be caused by inhomogeneous shear instability. Simultaneously we begin to see an extensive fusion and rotation of grains. This is reminiscent of “mechanical diffusion” (Ruoff, 1967) at a mesoscopic level due to slip and grain rotation. A fully developed pattern of turbulent-looking mixing is observed by Hammetter et al. (1988).

Evidence for grain rotation is fairly common among mixed powders when the constituents have a large impedance mismatch (e.g., Simonsen et al., 1992).

Fig. 4-20. Onset of flow instability and particle fusion in a Ni-coated aluminum powder at impact velocity of about 800 m/s.
In contrast to homogeneous media where slip may be the dominant mechanism of inhomogeneous deformation, heterogeneous powder mixtures may have an additional mechanism caused by the local curvature of the shock wave. According to Lighthill (1952) and Treusdell (1952), curved shocks in steady plane flow generate the vorticity, which is independent of the equation of state, given by

\[ \omega = -\frac{1 - \eta}{\eta} v_i \kappa \]  (96)

where \( \kappa \) is the curvature of the shock line, \( v_i \) the tangential component of velocity and \( \eta = \rho_0/\rho_1 \) is the density ratio across the shock front. Here, \( \rho_1 \) is the density behind the discontinuity.

In the above expression the term that depends on density change for powders is of the order of one. Hence, if the curvature is related to the average particle size of the mixture, then the vorticity may be viewed as the angular velocity impulsively imparted to the particle across the shock discontinuity.

To gain some qualitative appreciation of this vorticity, let us imagine a model where a powder mixture is represented by a collection of rigid circular disks having unit thickness as shown in Fig. 4-21. Then, depending on local conditions, some of the particles acquire a certain rotational kinetic energy as a wavy shock wave transverses this mixture. Subsequent motion of these disks is controlled by surface friction.

Consider the energy balance of the imparted rotational kinetic energy and the work done due to the circumferential surface resistance.

\[
\text{Rotational energy} = \frac{1}{2} I \omega^2 = \frac{\rho \pi}{16} D^2 (\omega R)^2
\]

\[
= (\pi D)^2 \sigma n = \text{work done by circumferential resistance.}
\]

Fig. 4-21. A schematic illustration of vortex generation in a particle aggregate behind a curved shock.
where \( I \) is the moment of inertia of the disk, \( \omega \) the impulsively imparted angular velocity, \( \rho \) the density, \( D (= 2R) \) the diameter of the disk, \( s \) the shear stress acting on the periphery of the particle, and \( n \) the number of total rotations. Additionally, it is assumed that the resistance acts on half of the circumstance to take into account void effect. Since the product \( \omega R \) may be replaced by relative particle velocity \( v \), the number of rotations may be approximated by

\[
n = \frac{\rho (\omega R)^2}{2^3 \pi \sigma} = \frac{\rho (kv)^2}{2^3 \pi \sigma} \tag{97}
\]

where \( k \) is a constant. It is interesting to note that the number of revolutions is independent of the diameter.

Similarly, the duration of a rotation can be estimated by effective deceleration to bring \( \omega \) to zero. That is,

\[
\omega = \dot{\omega} \times \Delta t \tag{98}
\]

where \( \dot{\omega} = M/I \) and \( M = \) the moment of the shear resistance given by

\[
M = \pi R^2 \sigma \tag{99}
\]

For the purpose of illustration, let us assume the following case:

\[
\rho = 8 \text{ g/cm}^3
\]

\[
kv = 1 \text{ km/s}
\]

\[
\sigma = 0.1 \text{ GPa}
\]

\[
D = 40 \mu m
\]

Then, upon substitution of these numbers into Eqs. (97) and (98), one finds

\[
n = 3
\]

\[
\Delta t = 8 \times 10^{-7} \text{s.}
\]

They are not unreasonable values for an explanation of the eddy-like mixing of powders under shock loading.
If both shear and vortex motions are activated under shock loading, then mass thinning called distributive mixing (see Fig. 4-22) may serve as an effective mechanism of mixing mass on the micro-crystallite level.

The curvature of a shock wave is not the only mechanism that leaves instability behind its front. There are other well known hydrodynamic instabilities that can occur under shock wave loading. They are, for instance, Rayleigh-Taylor, Helmholtz, and Richtmyer-Meshkov instabilities.

In explosive welding of metals as well as in oblique impact of high velocity bullets, wavy or vortex-like patterns are known to form at material interfaces. These features are thought to be associated with the classical Kelvin-Helmholtz instability in shear flow. In explosive welding, the formation of ripples is a key process parameter.

The Richmyer-Meshkov instability is one that is associated with impulsive, or shock-wave, acceleration of an interface of dissimilar materials. Several pairs of materials such as Cu/PMMA, and Teflon and Be, have been considered for possible R-M configurations under shock wave (Shaner 1984). It is quite possible that such an instability may be at work in mass mixing of powders on the submicronsecond level. Presently, however, these instabilities have not been applied to shock compression of powder materials.

It is our belief that instabilities of many kinds are closely associated with shock-induced chemical reactions. We hope that quantitative analyses will be

Fig. 4-22. An illustration of mass mixing due to a combination of slip and rotation.
developed in the future that include such effects as surface energy, material strength, and compressibility.

REFERENCES

Park, J. K., Ph.D., Thesis (unpublished), North Carolina State University, Raleigh, NC. 1975.


