SHOCK-WAVE
AND
HIGH-STRAIN-RATE
PHENOMENA
IN MATERIALS

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Shock Consolidation of Diamond

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Shock consolidation of powders with 10 to 50% of crystalline density of diamond and boron nitride, both pure and adhered with SiC and Sn/Cu whiskers and graphite, occurs upon application of 15 to 20 GPa. For powders, 10 to 100 μm in diameter, frictional sliding during shock consolidation gives rise to surface heating to temperatures of ~4000 K and results in a molten layer several μm thick. This molten layer fuses via heat conduction into the interior of the grain on a time scale short compared to the shock pulse duration. Using the theoretical model of comparison of Raizer and Shchelkin [1] for spherical or cubic grains, we estimate that the instantaneous work carried out against thermal energy in the sample is ~0.4% of the local shock energy. Therefore, most shock energy goes into surface heating. The recently reported consolidation of ~1 μm sized diamond powders is attributed to shock-induced melting and surface instabilities that result in a ductile extension of its melting line.

1 INTRODUCTION

The consolidation of diamond isothermally with carbon powder or additives has been achieved by the transformation of graphite to amorphous carbon which occurs above ~25 GPa as a result of graphite in the diamond fluid crossing the unstable extension of its melting line.

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technologically useful material. Diamond is the hardest material presently known with a micro-Vickers hardness of ~120 GPa. Sapphire (corundum) has a hardness of ~4500 GPa and single-crystal C-BN has a hardness of ~75 GPa. Diamond powders are typically both from natural and man-made sources. As a technological material, polycrystalline pure-facet-controlled diamond has many potential uses. In addition to those stemming from its high hardness, it is a direct consequence of its high longitudinal elastic velocity (18 km/sec) and thermal conductivity (6 W/cm °C). Similarly, hexagonal C-SiN, which is synthesized via plasma or dynamic high pressure does, have a high longitudinal wave velocity (16 km/sec) and thermal conductivity. C-BN is also more resistant to chemical reactions in an oxidizing environment at high temperatures than diamond. In addition, both cubic and hexagonal diamond powder [8], and the dense, nitrogen-rich, single-crystal C-BN may be synthesized (ca. 40 at% nitrogen, 60 at% carbon) by dynamic compaction from the graphite phase [9]. Nanometer-sized single-crystal domains exist as shock synthesized. This material may be shock consolidated [7]. Single-crystal powders of diamond and C-BN have been shock consolidated to a density of ~85% of theoretical density by driving shocks of ~15 to 30 GPa amplitude into samples within steel recovery containers.

Experiments in which SiC, SiCN whiskers, and graphite phase material are mixed with both diamond and C-BN are also reported [10, 11].

We review the different physical mechanisms which can give rise to shock consolidation, processes in these materials. We present a new analysis evaluating the energy partitioning upon shock compression assuming: 1) The energy of the shock waves all goes into melting a surface layer of the compacted particle. 2) The Hugoniot curve for the porous media is represented by the two straight lines 0Y and OC as an approximation to the porous Hugoniot OTB (Fig. 2). 3) The constant pressure specific heat (cp), melting temperature (Tm), and density (ρm) are independent of pressure

II. SURFACE HEATING MODEL

Precise modeling of the dynamic consolidation processes of porous metal powders [12, 13, 14] suggests that surface heating, by a particle-particle sliding produces a main layer of amorphous metal on each grain. This model is verified by microstructural observations of shock consolidated spherical, usually metallic, particles (e.g., [13, 15, 16] (Fig. 1) and by a large number of high-speed schlieren studies experiments on metals and non-metallic materials, as well as alpha-brass, 6061-T6, which demonstrates that interface melting occurs in virtual every medium [17].

The simplest model for energy partitioning upon shock compression assumes: 1) The energy of the shock waves all goes into melting a surface layer of the compacted particle. 2) The Hugoniot curve for the porous media is represented by the two straight lines 0Y and OC as an approximation to the porous Hugoniot OTB (Fig. 2). 3) The constant pressure specific heat (cp), melting temperature (Tm), and density (ρm) are independent of pressure
FIG. 1 Characteristic shape of shock consolidated, initially spherical powder. (A) Microphotograph of 37 μm diameter copper spheres dynamically compressed with a 5.6 GPa stress wave which propagated from right to left from Gorkin [13]. (B) and (C) copper sintering, 48 hr and 30 hr after 1000 m/sec stainless steel impact onto 30% porous steel rod. Arrows show shock consolidation morphology (from Williams and Eber [27]).

FIG. 2 Pressure-volume alarm sketch of principal isentrope, 01, and principal hypocentrope. 01, porous hypocentrope 1-100, and pore-collapse hypocentrope 0-0. Isentropes, principal hypocentrope, and porous hypocentrope pressure, P0, P1, P2 are indicated.
and temperature. Within these assumptions an upper bound to the mass fraction of metal in material is

$$L = \frac{P_0 V_e (V_{m} - V_e)(V_{m} + V_e)^{1/2}}{c_p V_e (T_m - T_e) + \frac{V_{m}}{\rho_m}}$$

(1)

where $T_m$ is the initial temperature and $V_{m}$ and $V_e$ are the specific volumes of the powder and crystal, respectively.

Some typical values, appropriate for the stock, consolidation of diamond (2) are $P_0 = 10$ GPa, $V_m V_e = 1.45$, $c_p = 7 \times 10^{6}$ erg$g^{-1}$K$^{-1}$, $T_m - T_e = 20000$ K, and $\rho_m = 3.2 \times 10^{12}$ erg$g^{-1}$ yields values of $L$ of 0.07.

Because calculations such as those shown in Figs. 1 and 2, in which 75 pm diameter 364 shishkebab rodions are assumed to be spherical solids, assume no horizontal sliding and heating, surface temperature of only 9600K, considerably less than 16000K cutting point of stainless steel, are calculated. The stresses within the interface of the rods are raised only to 460K. This is below the continuous shock temperature of $-500$K calculated for any porosity.

For spherical or near-spherical geometry, we calculate the magnitude of the irreversible work done against the material strength. Kakar and Chakrabarti (1) modeled the equiatomic cross-section of solid spheres packed in different geometries to infer the classification induced by crystal orientation. Although the isometric geometry of their model only approximates the characteristic orientation of particle deformation in shock compression, the initial packing density they examined for the hexagonal prismatic case is close to the initial density of many dynamic consolidations. For this reason, it is reasonable to adopt their spherical particle defects in Fig. 3. The cut volume of each particle of radius $R$ is given by

$$V_p = 4\pi R^3/3 - 2\pi R^2 (R - h) / 2$$

(2)

where $Z$ is the coordination number, and $h$ is the height of the flattened spherical segment. In terms of the radius of the flattened facet of the sphere of radius, $a$, this becomes

$$V_p = \frac{4}{3} \pi (R^3 - a^3) (a^2 - \frac{a^3}{2})^{1/2}$$

(3)

For equiatomic hexagonal prismatic deformation, $Z = 6$, $a = 0.949$ and $R = 4.8$. Deformation of spheres occurs with the facet circular faces on the prismatic surface. At this point the radius of the spherical particle has increased from $R_0 = 0.02033$ (which corresponds to $h = 0$ and $V_p = 1$) to $R_e = 0.04381$. At this point, solution of Eq. 2 yields $h_e = 0.036565$. As $R = R_0$ and $h = h_0$, the volume of a single is $V_e = 0.0187236$. Restretched to an initial radius, $R_0$, the initial facet height, $h_0$ is 0.003855. Use of Eq. (3) to calculate the
Initial and final flat radii, \( a_0 \) and \( a_f \), corresponding to \( R_0 \) and \( R_f \), yield \( a_f = 0.2182 \times 10^{-3} \) and \( a_0 = 0.322 \times 10^{-3} \). The bulk density becomes less than 61.4% of crystal density at \( R \) increases from \( R_0 = R_f \). Noting these values to calculate the principal strain as cylindrical overloads (see e.g. [14], p. 1:4) yields:

\[ \varepsilon_{bf} = \frac{2a_0 - a_f}{a_f} \approx 0.0236, \quad \varepsilon_{ic} = \frac{a_0 - a_f}{a_f} = 0.07054, \quad \text{and} \quad \varepsilon_{bf} = h_f / R_f = 0.1303. \]

The bar indicates average values between initial and final configurations. For an ideally plastic material, the stresses acting with these strains are equal within a multiplicative constant, of order unity, as the dynamic yield stress, \( \tau \). Thus, the plastic strain energy per unit volume of a spherical particle is

\[ E_{\text{plastic}} = \left[ \varepsilon_{bf} + \varepsilon_{ic} + \varepsilon_{rb} \right] \cdot V_c \cdot \tau \cdot Y / 2 \]

For \( Y = 8 \) and \( V_c = 0.4143 \), this yields: \( E_{\text{plastic}} = 0.0051 \times \tau \times V_c \cdot Y \).

We will now compare this plastic yield energy, \( E_{\text{plastic}} = E_{Y} (7, \tau, V_c, Y) \), for the diamond consolidation example given above. The diamond powder is, of course, actually...
small cubes, not spheres. Therefore, we expect the more deformable energy will usually be expressed than we calculate for a spherical case. In the present example, we see $V_0 = 0.5246 \text{ cm}^3$. 

Here $V_0$ is specific volume of diamond, $0.246 \text{ cm}^3/\text{g}$, and $0.5351$ is the density fraction corresponding to $k = k_0$. We also assume that $Y = 1$ or $10 \text{ GPa}$. Thus, $p_{\text{shock}} = 0.3 \times 10^7$ or $5 \times 10^7 \text{ erg/cm}^2$. This compares to $1.2 \times 10^9 \text{ erg/cm}^2$ by Eq. 10. Even if $Y$ is as large as $10 \text{ GPa}$, we infer that the shock energy is some 30 times greater than the deformation energy.

We conclude that most of the energy of the shock is, in fact, dissipated in sliding as in Eq. 1, and does not reside in deformational energy. However, for highly anisotropic powder (in) strain energy may play a more substantial role.

Given that a random layer forms on the surface of shocked particles or initially spherical or cubic shape, if dynamic consolidation is to be successful, the random layer must remain before area embalming takes place. What we envision is the extrusion surface of the original powder followed by the path indicated as "surface" in Fig. 4, whereas the lower schemes and start on the solid diamond transition labeled "interior" in Fig. 4. The time for cooling provides a valid constraint on the shock consolidation process. This time scale for cooling of free gas, $t$, of an initially solid layer of shock fraction, $L$, is given by (1).

$$t = \frac{5 \times 10^{-10} D_P^2 (T_0 - T_f)^2}{L}$$

(5)

![Diagram](attachment://diagram.png)

**FIG. 4** Phase relations for diamond and boron nitride. Shock consolidation to 15 GPa indicates thermodynamic pair of "interior" point achieves a temperature of 3000 K whereas "interior" point remains cold at principal bargain. Each path for thermal equilibrium is indicated.
where \( \kappa \) is the thermal diffusivity and \( d \) is crystal diameter. For \( \kappa = 1 \times 10^{-4} \text{ cm}^2/\text{sec} \), \( d = 120 \mu\text{m} \) and \( L = 0.5 \), we find \( t \approx 6.5 \times 10^{-3} \) sec. Thus, time is short compared to the duration of shock produced by the impact of a 1.5-mm-thick steel flyer plate used by the present authors and others. (Fig. 5) to conduct shock experiments. Moreover, the thermal conduction time: \( t_2 \approx 0.02 \text{ sec} \), is on the order of 10^(-6) sec for 1540 diamond crystals. As discussed by Peter and Ahrens [1], if the thermal conduction time equals the shock propagation time through the crystal: \( t_2 = t_0 \), heating of the sample should occur and samples are predicted not to consolidate via the equation of Fig. 4. Here, \( t_0 \) is shock velocity. For diamond, with \( v_0 = 15 \text{ km/sec} \), \( t_0 = 7 \) ns. However, samples with these grain sizes [7] do consolidate as discussed in Sec. III.

If the freezing time, \( t_4 \), becomes comparable with the shock duration time, \( t_1 \), in the sample, consolidation will not occur. For a shock duration of \( t_1 = 0.8 \mu\text{sec} \) solution of Eq. 5 yields a value of \( t_2 = 0.02 \mu\text{sec} \). Thus a larger crystal than this will consolidate only for longer shock duration.
III. SHOCK CONSOLIDATION OF DIAMOND VIA CONTINUUM HEATING

Recently, Sneyd and Naval [7], demonstrated that submicron sized diamond powders, made by either static or dynamic techniques, could be consolidated by shock heating to 20 to 25 GPa pressure. These powders had initial packing densities of 52 to 58% of crystal density. Since powders with values of less than 0.6 the bulk density achieve nearly continuous temperatures, is it possible that partially molten carbon is produced and given rise to the shock consolidation?

We calculate a continuum shock temperature with the usual equations:

\[ T_0 = T_0 + (T_f - T_0) \frac{V}{V_f} \quad (a) \]

\[ P_0 = \left( \frac{V}{V_f} \right)^{\gamma - 1} \left( \frac{\gamma - 1}{\gamma} \right) \frac{P_f}{\gamma} \quad (b) \]

\[ T_f = T_0 \exp \left( \frac{V_f - V}{V_f} \right) \quad (c) \]

\[ \frac{P_f}{\gamma} = \left( \frac{V_f}{V} \right)^{\gamma - 1} \frac{P_0}{V} \quad (d) \]

\[ T_0 = T_0 + V \frac{P_f}{\gamma} \left( \frac{P_0}{V} \right) \quad (e) \]

\[ P_f = \left( \frac{V_f}{V} \right)^{\gamma - 1} \left( \frac{\gamma - 1}{\gamma} \right) \frac{P_0}{V_f} \quad (f) \]

\[ \text{and} \]

\[ T_f = T_0 + V \frac{P_f}{\gamma} \left( \frac{P_0}{V} \right) \quad (g) \]

\[ T_0 = T_0 + \frac{V}{V_f} \left( \frac{P_f}{\gamma} \right) \quad (h) \]

**FIG. 6 Phase diagram of carbon.** Intersection of principal graphite-Hugoniot (n = 1.00) with heatstable extension of graphite melting line is predicted to induce formation of carbon glass. Graphite forms carbon glass upon static compression above 20 GPa as demonstrated by Gogotsi et al. [2/]. Regimes for porous diamond, with densities of \( n \) 1.43 and \( n = 1.92 \) are shown.
where $P_{yc}, V_{yc}$, and $T_{yc}$ are the pressure, (compressed) and initial volume, and temperature along the solid-solid, and $P_{yd}, V_{yd}$, and $T_{yd}$ are the same quantities along the porous\nHugoniot (Fig. 5). Also, $P_{s}$ and $T_{s}$ are the isentropic pressure and temperature at volume $V$.\nFrom the above, a new equation of state for porous diamond (20), the shock temperature for\nvarious values of diamond, $m = V_{yd} / V_{yc}$ for diamond were calculated and are shown in Fig.\n6. As can be seen, continuous temperatures of only $\approx 1500K$ are achieved in porous diamond\neven at larger $m = 1.9$. Plastic deformation can be achieved at such low temperatures as\ndemonstrated by the shock recovery experiments of Koizumi and Sawa (17). Recent\nobservations of plasticity in diamonds at 10 GPa and 1300K (21) are consistent with the\nplastic deformation consolidation experiments. We conclude that consolidation occurs as a result of\nformation of small quantities of melt, possibly the result of interparticle melting (e.g. 11, 15),\nfollowed by plastic deformation. The temperature and stress conditions required to induce\nplastic flow in diamond and C-BN are, however, not as well defined (e.g. 12, 13).

IV. SHOCK CONSOLIDATION OF DIAMOND VIA AMMIXTURE WITH GRAPHITE

Previous experiments (4) demonstrated that 13.16% graphite mixtures admixed with\ndiamond powders in the <5, 5/4, and 100-150um diamond range all resulted in enhanced\nconsolidation and conversion of graphite to diamond. Although at least 2 mechanisms for the\nenhanced compaction process for the admixture of graphite were previously suggested (4),\ntwenty Konharav et al. (28), reported carbon glass formation in room temperature in the 20\nto 30 GPa range. In analogy with the formation of graphite melt and SiC from the low\npressure phases as a result of crossing the metastable melting curve of H2O (29) (4) with\nspecific conditions and SiO2 crucible under static and dynamic conditions (25, 26), we observe\ngraphite, when mixed, also forms carbon glass, metastable, in the equilibrium field of\ndiamond. The Hugoniot temperature pressure relation of crystalline graphite as crosses the\nmetastable extension of the graphite melting curve at $\approx 25 GPa$ is shown in Fig. 6. Subsequent\nconversion of graphite to glass material, partial crystallization of diamond from the last phase\nis expected to occur and we believe this results in shock consolidation.

V. SHOCK CONSOLIDATION OF DIAMOND AND CBN VIA AMMIXTURE WITH SiC\nand Si3N4 WHISKERS.

Recently, Tan and Ahrens (30) and Yang et al. (31), have demonstrated that high\nquality dynamically consolidated material can be obtained when 1% to 35% SiC whiskers (SCW) and/or Si3N4 whiskers (SNW) are admixed with diamond and C-BN prior to\nconsolidation in the 15 to 20 GPa shock pressure range. Scanning (SEM) and transmission\nelectron microscopy (TEM) demonstrate that the SiCN or SNW are welded and reoriented
**FIG. 7** ESEM image of diamond (75%) plus SiC (25%) shocked to 21 GPa.

**FIG. 8** TEM observations on same sample as Fig. 7 (a) bright-field image of sub-micron SiC crystals (A) surrounding untransformed diamond crystal (B). (b) and (c) diffraction pattern from regrown (A) (lower) and (B).
in none overstressed materials. SCW and SNW have equal pressure melting points of 273 and 3100 K, respectively below the 4600 and 3600 K values for diamond and C-BN. Typical
sections are shown in Figs. 7-9 for material which was 70-75% diamond and 25-30% SCW
produced initially as 40% of crystal density. This mixture was shocked to ~20 GPa. From the
results of micro- and nano-indentation experiments, the SCW is assigned a lower bulk density; 40% of
crystal density, versus 71% for the diamonds [11]. We calculate from Eq. 1 that some 1% of the
diamond melted whereas 46% of the SCW is melted upon shock loading. The diamond
demonstrates both brittle and ductile deformation features. In general, the SCW is richer in the
form of sublimation-crystalline or amorphous. The effects of both pressure and temperature on the shock response of diamond, C-BN, SCW and SNW require further study.

VI. CONCLUSIONS

Experimental evidence, from shock-compressed spherical powder, indicates that the
deformation-energetic expended during shock consolidation is on the order of 0.4% of the
studied energy. Most of the energy dissipated upon shock consolidation of spherical and
(probably) cubic powder is dissipated as a result of grain boundary sliding giving rise to 5 to
10% most fractions of diamond and C-BN. Submicron powder seen in the 57% crystal
density images of Konrad and Banfill [7] active temperatures of ~1500K and consolidate
upon homogeneously deviated plastic deformation. Submicron aligned with graphite nanocluster via
the mechanism of graphite transmission to carbon glass upon repercussion to pressures
greater than ~20 GPa. Subsequent conversion of hot, amorphous material to diamond within its
stability field facilitates consolidation. Consolidations of diamond and C-BN with mixtures of SCW and BNW are bonded with melted and recrystallized whisker material. The extensive melting of the whisker material results favorable initial enhanced microporosity which occurs around the whisker material and the lower melting point of SCW and BNW, relative to diamond or C-BN. The deformation mechanisms under dynamic-compression require more study.

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