Shock consolidation of diamond and graphite mixtures to fused polycrystalline diamond

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The production of fused compacted polycrystalline diamond was achieved by subjecting porous (35%-49% porosity) mixtures of diamond crystals plus graphite (13-16 wt. %) to dynamic shock pressures of 10-18 GPa. The recovered material from an initial mixture of 4.8-μm diamond crystals plus graphite revealed a very homogeneous texture with little evidence of original grain boundaries. The preconsolidation addition of graphite also allowed ultrathin (≤5 μm) diamond crystals to be consolidated; this was not previously possible with the use of diamond crystals alone. The results are consistent with calculations which suggest that a thin layer of graphite surrounding a diamond crystal delays thermal equilibrium between the surface and interior of the diamond crystal, thus allowing greater surface heating. Consolidation is also probably enhanced by conversion of graphite to diamond, possibly via the liquid state.

I. INTRODUCTION

Previous experiments1-5 showed that the production of a fused polycrystalline solid compact, by subjecting an initially porous aggregate of diamond crystals to moderate-dynamic shock stress, depended critically on the size of the initial crystals. Ultrafine crystals (≤5 μm) did not fuse together, and it was assumed that this result was due to the fact that the time constant for thermal equilibrium between the surface and interior of the crystals approached the shock transit time through them, thus preventing local surface melting and consolidation. In the present study we describe the results of experiments which have shown that the initial addition of small quantities of very fine graphite to samples containing diamond crystals can be used to (a) consolidate fine diamond crystals and (b) produce more homogeneous fusion between larger diamond crystals (4-8 μm). We will show through model calculations that a thin layer of graphite covering diamond crystals effectively delays thermal equilibrium between the surface and interior of the crystals (because of the lower thermal diffusivity of graphite, as compared to diamond), thus allowing greater surface heating.

II. PHASE DIAGRAM OF CARBON

The details of the diamond/graphite equilibrium line have been known for some time, both from theoretical considerations6-10 and experimental synthesis of diamond from graphite. However, the exact nature of the melting lines of graphite and diamond have only recently begun to emerge. Venkatesan et al.11 and Tarasvist et al.12 used hydrogen graphite with a pulsed ruby laser at pressures of less than 0.1 GPa, and all experiments indicated a melting temperature of about 4300 K. In addition, the latter study indicated that the liquid evaporates at about 4700 K. The details of the slope of the melting line at higher pressures remain more controversial. Van Vechten13 used electroradiography as a sealing parameter to construct universal phase diagrams for group IV elements and binary alloys crystallizing in the diamond structure. His results for carbon are shown in Fig. 1(a) and predict that the melting line should have a negative slope of about -0.07 GPa/K. Experimental evidence10,14 showed that the melting line of diamond must come to the triple point (12.5-13 GPa, 4000-4200 K) with a slightly negative slope. Further evidence for this came from the behavior of small diamond crystals embedded in graphite rod specimens. It was found that there was a sharp temperature threshold at which the diamond crystals completely graphitized. By analogy with the direct graphite to diamond transformation, the flash-heating diamond graphitization line would be expected to be parallel to the diamond melting line, but a few hundred degrees cooler, and thus the slope of the line just above the triple point was inferred from that of the flash-heating diamond graphitization line.

Recently, Shaner et al.15 measured the sound velocity of graphite shocked into the high-pressure diamond field. These results are consistent with a phase diagram in which carbon (diamond) remains solid from 80 to 140 GPa along the Hugoniot curve16 along with the data points of Shaner et al.15 also shown in Fig. 1(a). Shaner et al. did not find evidence for a melting transition at any of those points, suggesting that the melting curve has a positive slope at high pressure. In Fig. 1(b) we present a proposed phase diagram for carbon which is basically an updated version of that developed by Bundy17,18 and by these recent observations and theory.

III. EXPERIMENTAL DETAILS

Shock compaction was achieved by using the flyer plate shock-wave generator and monequum trap recovery system shown in Fig. 2, which is a modified version of that given by Ahrens et al.19 A stainless-steel impactor plate, 1.5 cm in diameter and 0.25 cm thick (nickel) was accelerated to a velocity of between 1.81 and 1.87 km/s and impacted against a stainless-steel sample capsule containing the diamond crystals plus graphite sample which had been pressed into the sample ring and capsule. This produced a shock pulse with a duration of -0.8 μs. A 0.05-μm-thick film (single crystal) of Al2O3 (sapphire) was placed between the stainless-steel and diamond crystals (at the interface nearest to where the
of fusion between diamond crystals, [Fig. 3(c)]. This result contrasted to material recovered from previous experiments in which we unsuccessfully attempted to consolidate powdered <5 μm diamond crystals alone. The previous samples were very unconsolidated and showed no evidence of fusion.

2. Synthetic diamond crystals (4-8 μm) plus graphite (Fig. 4)

SEM analysis of the material recovered from shot 908 revealed a very homogeneous texture, with little evidence of original crystal boundaries [Fig. 4(b)], compare this with the initial crystals, Fig. 4(a)], much more so than previous compacts where the starting material was the 4-8-μm diamond crystals alone. However, the strength of the compact appeared to be slightly weaker than those recovered in the previous work.

B. Partially fused compact: Natural diamond crystals (100-150 μm) plus graphite

Analysis of the material recovered from shot 866 revealed a high degree of fracturing within the individual crystals [Fig. 5(b)], as was the case for previous compacts formed from large diamond crystals without graphite, and there was little evidence of fusion. The strength of the compact was only moderate, since particles could be removed with a sinter probe.

V. X-RAY ANALYSIS

Powder x-ray diffraction was performed by the Debye-Scherrer method with the use of a diamond D-500 diffractometer with CuKα radiation. Figures 6(a) and 7(a) show diffraction patterns of the original unshocked mixtures of the 8-5 μm diamond plus graphite and 4-6 μm diamond plus graphite. The 002 of graphite and the 111 and 220 d spacings of diamond are clearly evident. Figure 6(b) shows the diffraction pattern of the shocked <5 μm diamond plus graphite sample (shot No. 909). This shows that while the

D. J. Potter and T. J. Ahrens 911


FIG. 3. Thick compression of diamond experimental assembly.
diamond peaks remain, the graphite peak has substantially diminished. This suggests that much of the graphite has converted to diamond. The diffraction pattern of the shocked 4–8 μm diamond plus graphite sample from shot No. 908 (Fig. 7(b)) also exhibits a strong diamond graphite peak. Moreover, the broadening of the diamond (111) peak implies the presence of very small, crystallite sizes (10–20 nm). The Al₂O₃ peaks shown in this figure were due to small amounts of the remains of the Al₂O₃ disk which were unavoidably restored, along with the diamond, during the course of extracting a part of the sample for the analysis.

VI. MODEL CALCULATIONS

A. Continuum Thermodynamics

By using the shock (U_s) and particle (ν_s) velocity relationship of Pavlovskii for single-crystal diamond (3.51 Mbp/cm²),

\[ U_s (\text{km/s}) = 12.16 + 1.36\nu_s, \]  

(1)

the shock pressure (P_s) generated in single-crystal diamond, after passage of the shock wave through simulated 304 and an Al₂O₃ single crystal, was estimated by using the impedance matching technique. The projectile velocity was taken to be 1.82 km/s. The subsequent value of P_s generated in graphite (after passage of the shock wave through single-crystal diamond) was then calculated. Values were obtained for both single-crystal (2.26 Mbp/cm²) and porous graphite (initial density 55% of the crystal density) by using the following shock and particle velocity relationship:

\[ U_s (\text{km/s}) = 4.3 + 1.8\nu_s, \]  

(2)

FIG. 4. Scanning electron micrograph: (a) unshocked 4–8 μm diamond crystals; (b) fused diamond formed from >8-μm diamond crystals plus graphite (shot No. 908).

FIG. 3. Scanning electron image; (a) unshocked 4–8 μm synthetic diamond, (b) unshocked graphite, (c) fused compact (shot No. 908).

912 J. Appl. Phys., Vol. 6, No. 3, 1 February 1988
with the use of data from Mars[10] for values of $u_g$ in the range 0-2 km/s.

The shock (continuum) temperature $T_w$ was given by

$$T_w = T_e + P_e \frac{(P_g - P_e)}{\gamma C_v}$$

where $T_e$ and $P_e$ are the temperature and pressure along the principal inertias, $P_g$ is the high-pressure specific volume, $\gamma$ is the Grüneisen parameter (taken to be 0.9),[12] and $C_v$ is the specific heat at constant volume (assumed to be $3\gamma \Gamma$, where $\Gamma$ is the gas constant and $M$ is the atomic weight).

Values of $T_w$ are given in Table II and plotted in Fig. 1(b). The results indicate that higher temperatures are generated in the graphite (particularly if it is porous), but these are only a few hundred degrees higher than those generated in the diamond and wet below those required for melting.

Since these temperatures are some 3000 K below the melting line of diamond, we conclude that absolute lower bounds and that achievement of higher temperatures can only be the result of local inhomogeneous heating. The concept was suggested by De Carlo[13] for the shock production of diamond from an initially porous graphite. We assume that grain-boundary sliding is the main mechanism for generating the necessary temperatures to produce partial melting in the fused compacts. However, netting and irregular reflection probably also occur. Note that under the above conditions, graphite is shocked into the diamond regime.

B. Time scales for heat flow

There are at least three time scales of interest which may be calculated with simple one-dimensional assumptions in

![Fig. 6. Debye-Scherrer diffraction patterns, show 998: (a) initial graphite (G) plus diamond (D) mixture; (b) postshock pattern.](image)

![Fig. 7. Debye-Scherrer diffraction patterns, show 998: (a) initial graphite (G) plus diamond (D) mixture; (b) postshock pattern.](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Shock pressure ($P_s$) (GPa)</th>
<th>Shock temperature ($T_e$) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single-crystal diamond (1.53 g/cm³)</td>
<td>40.0</td>
<td>590</td>
</tr>
<tr>
<td>Single-crystal graphite (2.26 g/cm³)</td>
<td>29.6</td>
<td>610</td>
</tr>
<tr>
<td>Porous graphite (55% of single-crystal density)</td>
<td>7.9</td>
<td>910</td>
</tr>
</tbody>
</table>

* Initial shocked states.

D. K. Pope and T. J. Ainscow, 913
the present experiments. These are (1) the time scale of freezing of a layer of L class fraction of molen material, \( t_c \); (2) the time scale required to heat and melt, via frictional sliding at other mechanisms in the molen and Fourier conducting into the interole, the entire crystalite that achieving an approximately uniform temperature, \( t_c \); and (3) the nine scale of shock-wave propagation through the crystal, \( \tau \). The latter time scale, that we might infer may be on the order of the period of frictional heating of the surface, although other processes such as joining and angular rectification may also assist in production of melt.

The time scale for freezing, \( t_c \), is initially no longer than that of molen fraction \( t_c \), as given by the theory of Schwartz et al. \(^\text{[4]}\)

\[
\tau = \frac{\eta}{\Omega}[\rho H_\ell (\rho / C_p) (T_c - T_s)]^2
\]

where \( \eta \) is the thermal diffusivity of diamond, \( \omega = (\pi / 2)^2 \) m/s, \( \rho \) is the density of diamond, \( H_\ell \) is the heat of fusion (9.2 MJ/kg), \( C_p \) is the specific heat at constant pressure (\( 2.5 \) J/g K), and \( T_c - T_s \) is the temperature difference between melting and ambient temperature (\( 500 \) K). For \( d = 10 \) \( \mu \)m and \( L = 0.05 \), \( \tau = 6.5 \times 10^{-10} \) s. This time is very short compared to the thermal equilibrium time which from

\[
t_c = \frac{\rho}{\Omega} \frac{d^3}{\tau}
\]

where we assume a mean shock velocity of \( 15 \) km/s. This size range of crystal appears to shock consolidate best either with graphite or without. As noted earlier \(^1\), when the initial crystal size becomes small, the value of \( t_c \) decreases, and we infer that the crystal expands heat from the surface rapidly as they become more isotropical. (Shock welding appears to occur in \( \leq \) 50 \( \mu \)m crystals without graphite under our experimental conditions.) The critical crystal sizes are obtained from setting \( t_c = 0.007 \) s.

As partial fusion of the \( \leq 5 \) \( \mu \)m sample is observed (see Table 1), two mechanisms are expected to be at work, causing enhanced fusion of the diamond crystals.

We believe that as graphitization is a heat transfer, with respect to diamond with \( D = 10^{-10} \) m/s it provides a thermal insulating layer between diamond crystals during shock consolidation, and this allows for more of the material to be heated to the melting point during compaction. For example, a 0.1 \( \mu \)m-thick layer of graphite around a 10-\( \mu \)m diamond crystal will have a thermal equilibrium time of \( 10^{-11} \) s, this is much longer than the freezing time of \( 5 \times 10^{-10} \) s calculated from Eq. (4). In addition, some of the graphite appears to convert to diamond, possibly partially from the liquid state. Substantial, but not complete, conversion from graphite to diamond is demonstrated in Figs. 6 and 7.

**VII. CONCLUSIONS**

We conclude that mixing a small quantity of graphite with diamond upon shock consolidation effectively design...