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SHOCK COMPRESSION OF DIAMOND CRYSTAL

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Abstract. Two shock wave experiments employing inclined mirrors have been carried out to determine the Hugoniot elastic limit (HEL), final shock state at 191 and 217 GPa, and the post-shock state of diamond crystal, which is shock-compressed along the intermediate direction between the <111> and <110> crystallographic axes. The HEL wave has a velocity of 19.9 ± 0.3 mm/μsec and an amplitude of 63 ± 28 GPa. An alternate interpretation of the inclined wedge mirror streak record suggests a ramp precursor wave and then another HEL value. The maximum post-shock density achieved upon release from the ~200 GPa shock state is ~3.95 Mg/m^3, which compares to the initial density 3.52 Mg/m^3. This result suggests an elastic unloading effect or shock-induced transition to a denser (possibly metallic) phase.

Introduction

The high pressure equation of diamond is of geophysical interest because of the likelihood that the proposed post-diamond metallic phase of carbon [see e.g. Bundy, 1980] is stable at lower mantle and core pressures implying high solubilities of C in the earth's iron core. Previously, Pavlovskii [1971] reported four Hugoniot data for single crystal diamond to 590 GPa and five data for porous samples (ρ_0 = 1.90 Mg/m^3), whereas McQueen and Marsh [1968] reported the Hugoniot data for pressed diamond (ρ_0 = 3.191). Other investigations of the high pressure phase diagram of carbon have utilized shock-compression studies on graphite or carbon with various densities [Grover, 1979, and Bundy, 1980]. The object of the present work was to carry out a reconnaissance study of the dynamic yielding stress and search for evidence of the metallic phase transition.

Experimental

The two natural, industrial diamond samples (4.7 carat and 8.9 carat for shot #106 and shot #108, respectively) used in this study were transparent but contained cracks and brown inclusions. Bulk densities of the samples, which were measured by an Archimedean method using toluene at 21.6°C, were 3.516 ± 0.005 and 3.519 ± 0.003 Mg/m^3, respectively, which closely agrees with the X-ray density of 3.515 Mg/m^3. The crystallographic directions of the sample surface for both crystals were determined by the X-ray Laué technique. The normal axis to the sample surface of both crystals were very close to each other and inclined 15.4 ± 0.6° from <111>, or 29.6 ± 0.6° from <110> in approximately the (110) plane. The normal axis to the sample surface was actually inclined 1.5 ± 0.2° from the (110) plane. Longitudinal sound velocity measured at ambient pressure and temperature using a pulse transmission technique was 18.13 ± 0.41 mm/μs. Using McSkimin and Andreatch's [1972] elastic moduli, the calculated longitudinal sound velocity in the same crystallographic direction as these samples was 18.57 mm/μs, which was in reasonable agreement with the observed value.

The two samples were mounted on OFHC copper and tantalum driver plates, 0.6 mm thick, respectively. Four flat mirrors and inclined wedge-mirrors were mounted on the sample assemblies in order to measure shock wave and free surface velocities [Ahrens, 1980]. The wedge mirrors with appropriate angles for shot #106 and #108 were placed at the inclined angle of 9.62° and 6.24°, respectively. Self-shorting pins were also mounted on the sample assemblies to measure shock-wave velocity using an oscilloscope. The target assembly for shot #106 and #108 samples were respectively impacted by Cu and Ta flyer plate imbedded on a lexan sabot accelerated by a 25 mm bore diameter two-stage light-gas gun. The projectile velocity was measured by a flash X-ray shadowgraph technique [Jeanloz and Ahrens, 1977]. Shock and free-surface velocities were measured by using an image converter streak trace. The time calibration of the writing rate was obtained using a Pockel's-cell modulated Argon laser beam with 30.0 MHz timing marks [Jeanloz and Ahrens, 1977]. Self-shorting pins were connected to a RC pulse circuit, which utilized a tilt-pin technique [Kondo et al., 1981] in order to identify which pins were activated.

Results and Discussion

The streak camera records for both experiments suggest a double-wave structure in diamond sample. The streak trace of the inclined mirror clearly detects the first shock arrival. The slope of the inclined mirror image is used to obtain the accompanying free-surface velocity. The particle velocity behind the first wave was obtained using the free-surface approximation [Wackerle, 1962]. The reflectivity at the flat arrival mirror is not completely lost upon the first shock-wave arrival. At the second (final) shock-wave arrival, the reflectivity of the arrival mirror is completely destroyed. The self-shorting pin also recorded this wave arrival. The bending point of the inclined mirror streak trace, taking into account of the free-surface motion due to the first shock arrival, is consistent with both the arrival mirror and shorting-pins result (within an experimental error). The impedance-match method was used to obtain the final shock state,

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employing shock wave data for the standard materials (Cu and Ta) [McQueen et al., 1970]. The experimental conditions and results are summarized in Table I.

The present results and Pavlovskii's data or diamond crystal and his linear expression [1971] are shown in Fig. 1. The shock pressure versus density relationship of the present data and the data of [Pavlovskii, 1971, and McQueen and Marsh, 1968] are also plotted in Fig. 2. The second order Murnaghan-Birch isentropic equation of state for diamond is calculated on the basis of ultrasonic data [McSkimin and Andreatch, 1972]. We use 442.3 GPa and 4.03 for the bulk modulus and its pressure derivative, respectively.

Since the first shock velocity is close to and slightly higher than the longitudinal sound velocity, the first wave is possibly an elastic wave and the data points correspond to the Hugoniot elastic limit (HEL) of diamond which appears to be as high as 63 ± 28 GPa. This value of the HEL is the largest one observed for any solid. Using the offset between the HEL (σ_H) and mean (hydrostatic) pressure (P), the shear strength (τ^*) is [Graham and Brooks, 1971];

$$\tau^* = \frac{3}{4} (\sigma_H - \bar{P}),$$

This yields a value of 30 GPa. The theoretical strength of (perfect) diamond crystal has been calculated to be 92 GPa for the <110> {111} slip direction [Tyson, 1966] or 121 GPa [Kelly, 1966]. For silicon crystal, the theoretical strength is calculated to be 14 GPa [Kelly, 1966] and the shear strength estimated from HEL [Gust and Royce, 1971] is 2 and 3 GPa for <110> and <100>, respectively. The ratio of the observed shear strength to the theoretical one for diamond is considerably larger than that for silicon, but in good agreement with it in order of magnitude. If loading is accomplished in a direction which causes no shear on a potential slip plane, failure cannot be expected by conventional slip mechanisms. Experimental evidence for this is shown in the case of silicon, where larger HEL values for <100>, 9.2 ± 1.0 GPa should be compared to 5.0 ± 0.5 and 5.4 ± 0.3 GPa for <110> and <111>, respectively. By analogy, the maximum HEL value of diamond can be estimated to be about 110 GPa in the <100> direction.

We note that the inclined mirror streak trace between the first shock and the final shock arrivals is not distinct. Moreover, the reflectivity decrease of the flat arrival mirror is not pronounced upon the first shock arrival. Since as in Pavlovskii's experiments, the self-shorting pins did not respond to the first wave either. Our observations suggest that a ramp rather than an elastic shock wave is generated. If this is really the case, the inclined mirror trace could be interpreted as actually being convex in shape and $U_s - U_p$ relationship could have a negative slope. The HEL then would be of another value. Such a ramp wave is observed upon compression of four-fold coordinated covalent materials, for example, fused quartz [Wackerle, 1962], SiC [McQueen et al., 1970], and AlN [Kondo et al., 1982].

To determine the final shock state, the impedance match method centered on the first shock state was used in the present analysis. Since

TABLE I. Summary of Shock Compression of Diamond

Shot Number	Flyer & Driver Plate	Projectile Velocity [mm/μs]	Initial Density [Mg/m³]	Sample Thickness [mm]	First Shock State: Shock Velocity [mm/μs]	First Shock State: Particle Velocity [mm/μs]	First Shock State: Shock Pressure [GPa]	First Shock State: Density [Mg/m³]	Final Shock State: Shock Velocity [mm/μs]	Final Shock State: Particle Velocity [mm/μs]	Final Shock State: Shock Pressure [GPa]	Final Shock State: Density [Mg/m³]	Post Shock State: Free Surface Velocity [mm/μs]	Post Shock State: Post Shock Density [Mg/m³]
106	Cu	6.106	3.516	3.404	20.1	0.90	63.6	3.681	14.55	3.425[a]	190.5	4.516	5.984	3.909
		±0.005	±0.005	±0.036	±0.8	±0.34	±27.7	±0.057	±0.30	±0.082	±8.8	±0.099	±0.100	±0.174
108	Ta	5.871	3.519	5.380	19.61	0.899	62.0	3.688	15.90	3.703[a]	217.1	4.536	6.26	3.991
		±0.005	±0.003	±0.074	±0.32	±0.063	±5.3	±0.016	±0.30	±0.025	±3.6	±0.030	±0.97	±0.408

[a] impedance match solution

Pavlovskii's analysis did not include the offset due to the HEL, we show (Fig. 2) for comparison to Pavlovskii, our points for the final state calculated via his method (impedance-match method centered at ambient conditions and ignored the HEL). The data reduced in this way yield a slightly greater compression than predicted by the hydrostat. This treatment would more closely correspond to an elastic-completely plastic material whose shear strength was completely relaxed [Graham and Brooks, 1971].

The free-surface velocities (U_{fs}) from the final state for both shots are less than twice the shock-state particle velocity (U_p), which is estimated by the impedance match solution. These differences are comparable to or slightly larger than effect of possible elastic unloading on the rarefaction wave. Therefore, we could not identify with certainty which effect, elastic unloading or possible irreversible phase transition, produce this result.

If isentropic rarefaction from the high-pressure shock state can be assumed, a constraint on the maximum postshock densities of 3.91 ± 0.17 and 3.99 ± 0.41 Mg/m^3 are obtained (Table I) [Lyzenga and Ahrens, 1978]. The comparison, the crystal density of diamond is 3.52 Mg/m^3, whereas, the reference densities in the standard state for Grover's [1979] and Van Vechten's [1973] models for metallic diamond are 3.75 and 4.65 Mg/m^3, respectively.

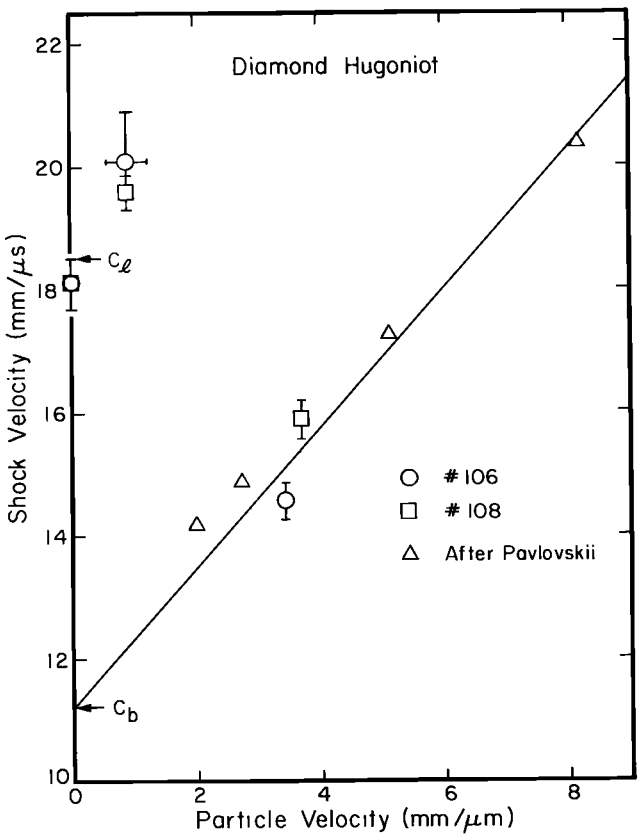

Fig. 1 Diamond Hugoniot in shock velocity (U_s)-particle velocity (U_p) coordinates. C_l and C_b denote longitudinal and bulk sound velocities (18.57 and 11.22 mm/μs, respectively) calculated from McSkimin and Andreatch [1972] data. Present longitudinal velocity at zero pressure is also shown. Pavlovskii [1971] data are obtained using single crystal diamond with the initial density of 3.51 Mg/m^3.

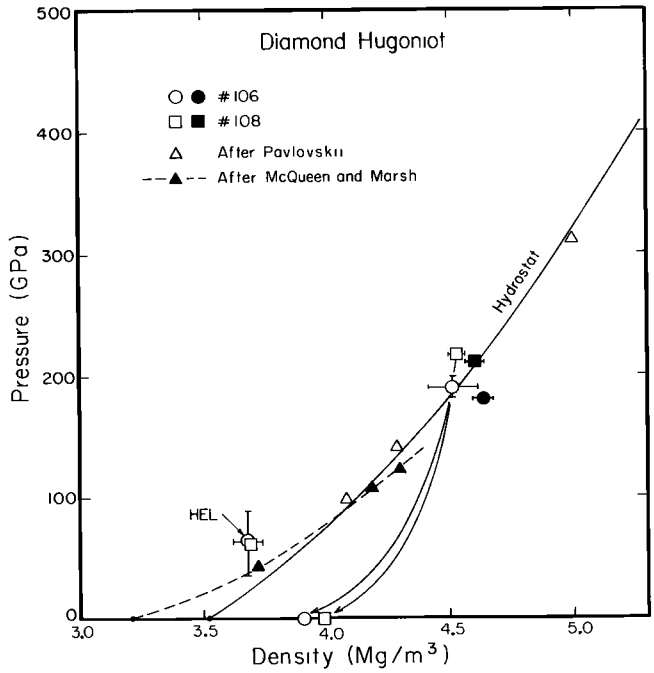

Fig. 2 Pressure versus density Hugoniot and release wave paths for diamond. Open circle and square states take HEL state into account while solid circle and square states are calculated neglecting the HEL state as in the Pavlovskii procedure. Hydrostat is estimated using McSkimin and Andreatch [1972] ultrasonic data. The initial density of pressed diamond is 3.191 Mg/m^3 [McQueen and Marsh, 1968]. The highest pressure point of Pavlovskii [1971] is at 585 GPa, 5.874 Mg/m^3, and does not appear in the figure.

The two Hugoniot points of the pressed diamond [McQueen and Marsh, 1969] in Fig. 3 are located below the theoretical principal isentrope (hydrostat). The Hugoniot pressure of a porous material without phase transition can be estimated using Mie-Grüneisen equation of state and thermodynamical parameters. Since the thermodynamically determined Grüneisen parameter is ~0.9 at ambient conditions [Pavlovskii, 1971], the porous Hugoniot data [McQueen and Marsh data, 1968], should lie at higher pressures than the (hydrostat) isentrope. For example, at the maximum compression state the hydrostat for the crystal is 30 GPa higher than that for porous material. Thus the porous diamond data provide some support for the hypothesis of a shock-induced transition to a high-pressure probably metallic phase.

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