SHOCK COMPRESSION, ADIABATIC EXPANSION
AND MULTI-PHASE EQUATION OF STATE OF CARBON

Konstantin V. Khishchenko¹, Vladimir E. Fortov¹, Igor’ V. Lomonosov²,
Mikhail N. Pavlovskii³, Gennadii V. Simakov³, and Mikhail V. Zhernokletov³

¹Institute for High Energy Densities, RAS, Izhorskaya 13/19, Moscow 127412, Russia
²Institute for Chemical Physics Research, RAS, Chernogolovka 142432, Russia
³Russian Federal Nuclear Center – VNIIEF, Sarov 607190, Russia

Abstract. The compressibility of graphite and diamond samples of various initial densities has been studied experimentally in shock waves at pressures in the range 5–74.5 GPa. The states of graphite samples have been investigated also under reflected shock loading up to 182 GPa and in adiabatic release waves at pressures down to 4.5 GPa. A semiempirical equation-of-state model, which takes into account the effects of polymorphs transformation and melting, is proposed. An equation of state is developed for the graphite, diamond, and liquid phases of carbon, and the critical analysis of calculated results in comparison with the newly acquired and available high-energy-density experimental data is made.

INTRODUCTION

The multi-phase equation of state (EOS) of carbon over wide range of pressures and temperatures is required for numerical simulation of hydrodynamic processes under extreme conditions of high energy densities [1–3].

In the present study we have obtained data on the compressibility of graphite and diamond samples of various initial densities in shock waves at pressures in the range 5–74.5 GPa. We also have measured the states of graphite samples under reflected shock loading up to 182 GPa and in adiabatic release waves at pressures down to 4.5 GPa. We propose the semiempirical EOS model, which takes into account the effects of polymorphs transformation and melting. EOS is constructed for the graphite, diamond, and liquid phases of carbon on the basis of the model developed. The critical analysis of calculated results in comparison with the newly acquired and available high-energy-density experimental data is made.

EXPERIMENTAL METHODS AND RESULTS

The samples we investigated experimentally consisted of synthetic diamond with initial densities \( \rho_{01} = 2.02, 1.789, 0.607, \) and 0.56 g/cm\(^3\), and graphite with \( \rho_{02} = 1.87 \) g/cm\(^3\). Shock waves were generated in the samples through copper, aluminum, or iron plates by steel projectiles accelerated by the detonation products of condensed explosives up to velocities of 5–6 km/s. By recording the velocity of the shock front \( U_s \) (with an error of \( \sim 1.5 \) %) in the samples, we were able to define the particle velocity \( U_p \) and pressure \( P \) [4] based on the known Hugoniot equation of the plate material and the preset parameters of the shock waves generated in them. Measurements were taken by an electric contact basis method; the signals from the detectors were displayed on a fast oscilloscope. The experimental data averaged over six to eight recordings are presented in Fig. 1.

The data obtained from the samples of graphite and diamond with densities \( \rho_{00} = 2.02–1.789 \) g/cm\(^3\)
FIGURE 1. Shock Hugoniot of diamond and graphite samples with initial densities $\rho_0 = 1.87$ (a, c), 2.02 (b), 1.789 (d), 1.011 (e), 0.607 (f), and 0.56 (g) g/cm$^3$. Solid lines correspond to results of calculation for diamond, dashed lines — for graphite. Experimental data: 1 and 2 — this work, 3 — [5], 4 — [7, 8], 5 — [9].

FIGURE 2. Shock Hugoniot (a), curves of second shock compression (b–d), and release isentropes (e–h) of graphite samples with initial density $\rho_0 = 1.87$ g/cm$^3$. The notations are analogous to Fig. 1.

agree satisfactorily with the results of previous studies of the shock compression of porous natural diamond samples of $\rho_0 = 1.9$ g/cm$^3$ [5] and graphite samples of $\rho_0 = 1.768–1.878$ g/cm$^3$ (above the region of shock-induced graphite-to-diamond transformation) [6–9]. An analogous conclusion follows for the data obtained from the diamond samples of $\rho_0 = 0.56$ g/cm$^3$ in comparison with the data for foamed carbon with the same initial density from Ref. [9].

In experiments where we studied reflected shock and adiabatic release waves, the measured quantity was shock velocity $U_s$ in barriers with various dynamic impedances placed after the samples, allowing us to determine the parameters of the final states. A number of points on the second shock adiabats were obtained by reflection from barriers that were more rigid than graphite and with known Hugoniot (tungsten, tantalum, copper, zinc, and titanium). The region of decreased pressure was studied using soft dynamic barriers (polymethylmethacrylate, polyethylene, and foamed polystyrene with various initial densities), the shock Hugoniot of which are also known [10].

In order to monitor the parameters of the original states, in the majority of experiments on graphite samples with diameter 40 mm and thickness 2.5 mm we used both cylindrical tablets made of barrier materials with dimensions 12 and 3 mm respectively and tablets made from graphite itself. The determined values of pressure behind first shock front are $P = 13.4$, 23.1, 42.5, and 51.4 GPa. A detailed description of the methods and components used to perform the experiments is contained in Ref. [10]. The experimental data for second shock compression and adiabatic expansion of graphite averaged over five to seven independent recordings are presented in Fig. 2.

**EOS MODEL**

According to the EOS model, the Helmholtz free energy for matter is preassigned as a sum of three components

$$F(V, T) = F_c(V) + F_a(V, T) + F_e(V, T),$$
describing the elastic part of interaction at $T = 0$ K ($F_c$) and the thermal contribution by atoms ($F_d$) and electrons ($F_e$).

The selected form of $F_c$ for the solid phases [11] provides for the correct values of the cohesive energy $E_{coh}$ in the limit of $V \rightarrow \infty$, and the bulk compression modulus and its pressure derivative under normal conditions [12, 13], as well as agreement with results of calculation [14] using the corrected Thomas–Fermi model in the range $V_{0c}/V = 20-500$ (where $V_{0c}$ is specific volume at $P = 0$, $T = 0$ K).

The lattice contribution to the free energy of the solid phases is defined by excitation of acoustic and optical modes of thermal vibrations of atoms

$$F_a(V, T) = F_{a}^{\text{act}}(V, T) + \sum_{\alpha=1}^{3} F_{a\alpha}^{\text{opt}}(V, T),$$

$$F_{a}^{\text{act}}(V, T) = \frac{RT}{\nu} \left[ \ln \left( 1 - e^{-\theta_{ac} / T} \right) - D \left( \theta_{ac} / T \right) \right] - \beta_{ac} \frac{T^2}{\theta_{ac}} \frac{\theta_{ac}}{e^{\theta_{ac} / T} - 1},$$

$$F_{a\alpha}^{\text{opt}}(V, T) = \frac{RT}{\nu} \ln \left( 1 - e^{-\theta_{opt} / T} \right) - \beta_{\alpha} \frac{T^2}{\theta_{\alpha}} \frac{\theta_{\alpha}}{e^{\theta_{\alpha} / T} - 1},$$

where $R$ is the gas constant, $\nu$ is the number of atoms in an elementary cell of the lattice, $D$ is the Debye function [15], $\theta_{ac}$ and $\theta_{opt}$ are the characteristic temperatures of acoustic and optical modes of phonon spectrum [16]. The last terms in expressions for $F_{a}^{\text{act}}$ and $F_{a\alpha}^{\text{opt}}$ take into account the effects of anharmonicity of thermal lattice vibrations. These terms are exponentially small at low temperatures and provide for behavior of heat capacity $C_V \sim 3R - T^2$ at $T \rightarrow \infty$ [17]. The coefficients $\beta_{ac}$ and $\beta_{\alpha}$ are found from high-temperature data for enthalpy of graphite under the normal pressure [18].

The electronic component of the free energy of the graphite phase is given by the expression

$$F_e(V, T) = -\frac{1}{2} \beta_0 T^2 \sigma^{-\gamma_0},$$

where $\beta_0$ is the coefficient of electronic heat capacity at $T = 0$ K [17], $\gamma_0$ is Gruneisen coefficient under normal conditions.

The electron contribution to the free energy of diamond, which is a dielectric with the energy gap between the valence and conduction bands $\Delta_0 \approx 5.5$ eV [19], is negligible in comparison with $F_e$ at temperatures $T \ll \Delta_0/k$ (where $k$ is Boltzman constant). Therefore $F_e = 0$ for the diamond phase.

The free energy $F$ of liquid carbon has the form of thermodynamic potential of the liquid phase in the EOS model [1].

**RESULTS OF CALCULATIONS**

As follows from Fig. 1 and 2, the multi-phase EOS constructed for carbon adequately describe the experimental data obtained in this work and previously [5, 7–9] over the entire range of dynamic characteristics generated in shock-loading and adiabatic release waves.

The adequacy of the proposed form of contribution of thermal lattice vibrations to the thermodynamic potential is illustrated by Fig. 3, in which the calculated values of isobaric heat capacity of graphite and diamond under the atmospheric pressure are compared with experimental data [17, 20].

An analysis of the results of measurements of sound velocity in shock compressed graphite with $\rho_0 = 2.2$ g/cm$^3$ [21] indicates that carbon is in the solid diamond phase at pressures in the range 80–143 GPa. On the calculated shock Hugoniot of the
FIGURE 4. Phase diagram of carbon. \( M \) — diamond melting curve, \( a-g \) — shock Hugoniots of carbon samples with initial densities: 1 — 3.51, 2 — 3.191, 3 — 2.2, 4 — 2.02, 5 — 1.87, 6 — 1.789, 7 — 0.56 g/cm\(^3\). The level of pressures realized in experiments: 1 and 2 — this work, 3 — [5], 4 — [9], 5 — [21].

Graphite with that initial density melting of diamond begins at \( P \approx 150 \) GPa, and this value is consistent with experimental data [21].

The phase diagram of carbon calculated on the basis of the developed EOS is shown in Fig. 4. It reveals a region of states realized in the shock-wave experiments with traditional explosives systems [5, 6, 9] and a two-stage light-gas gun [21]. As can be seen, the data obtained in this work correspond to both solid and liquid phases of carbon.

Thus, the multi-phase EOS we have constructed for carbon describes consistently the collection of the newly acquired and available experimental data, and it can be employed effectively in numerical simulation of hydrodynamic processes at high energy densities.

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