

## **Diamond Production as a Result of Electrical Explosions of Graphite-Containing Samples<sup>1</sup>**

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A method to achieve the region of thermodynamic stability of diamond is described. Pressures in the range 10–30 GPa and temperatures in the range 2000–4000 K may be obtained by current pulse heating of a special graphite-containing sample. Numerical modeling of some regimes of capacitor bank discharge through the sample showed that this is possible by current pulses with a duration 2–10  $\mu\text{s}$  and a magnitude of about 1 MA and higher. In doing so, the conductivity of the sample is of great importance. The analysis of numerical modeling results indicates that the best values of diamond synthesis parameters are achieved for metallic samples. Nonporous material containing small graphite particles having a size in the range of 10–100  $\mu\text{m}$  was used. The best results are achieved when graphite constitutes no more than about 30% by volume of the sample. The method was tested under laboratory conditions. In these experiments, hexagonal diamond particles were obtained. The mean size of diamond crystallites was about 0.1–0.2  $\mu\text{m}$  or smaller.

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**KEY WORDS:** artificial diamond; exploding wire method; high pressures; high temperatures.

### **1. INTRODUCTION**

The recent decade has seen the development of essentially three methods for producing diamonds by subjecting graphite to high pressures: static conversion without catalyst, conversion with use of catalyst, and shock synthesis.

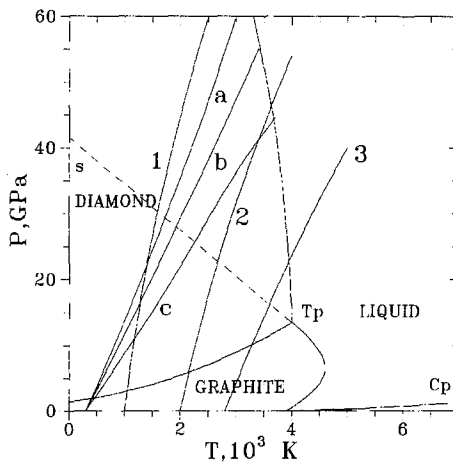
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A successful static conversion without catalyst was carried out by Vereschagin [1]. He used a steady-state method, while Bundy [2] synthesized diamonds without the use of catalyst in static high-pressure flash heating experiments. The transformation can take place at pressures of 12–18 GPa and temperatures of 2800–4100 K (see phase diagram of carbon in Fig. 1). The effective duration of these conditions was about 20 ms [2]. The product of this synthesis was polycrystalline diamond having an average crystallite size of about 100 nm. The use of a catalyst such as molten Fe, Co, Ni, or Pt appears to increase the diamond growth rate and to decrease the transformation pressure and temperature.

At the present time, a significant amount of diamond is produced by the explosive shock method. The first successful diamond synthesis under dynamic conditions without catalysts or seeds was achieved by De Carli and Jamieson [3] and, almost contemporaneously, by Alder and Christian [4]. The Hugoniot data indicate that significant conversion to diamond should begin at shock pressures of 22–24 GPa. The carbon density has an influence on the effective shock pressure range. Lower densities ( $0.45\text{--}1.7\text{ g}\cdot\text{cm}^{-3}$ ) give higher yields of diamond under conditions producing lower shock pressures (as low as about 20 GPa), whereas pressures of about 70 GPa are preferred when density is high. The usual product of



**Fig. 1.** Carbon phase diagram [2]. 1, 2, and 3 are Hugoniot data for pyrolytic graphite; a, b, and c are Hugoniot data for porous diamond with a porosity of 1.54, 1.68, 1.93, respectively [6]. Here  $T_p$  is the triple point,  $C_p$  is the critical point, and  $s$  is the line of fast graphite-to-diamond transformation.

shock synthesis of diamond consists of polycrystalline particles. These particles have diameters ranging from about  $10\ \mu\text{m}$  and smaller and have crystallite sizes in the range of 10 to 20 nm. The inference from Hugoniot data was that diamond formation occurred on a time scale comparable to the rise time of the shock wave (about of  $10^{-8}$  s).

The present paper reports some results of diamond formation by means of a high-powered capacitor bank discharge, from which an electric current flows through a graphite-containing sample. In the first part of the paper we present results of numerical modeling of such processes. This investigation permitted us to find out discharge circuit parameters and sample sizes by which dynamic synthesis conditions can be created. We considered discharge circuits producing current pulses of up to 2 MA and a duration in the range of 1–10  $\mu\text{s}$ . In the second part of the paper, we present preliminary experimental results.

## 2. THEORY

Let us consider a discharge of a capacitor bank through a sample in the form of a rod. Let the rod length  $l$  be much larger than its radius  $a$ . In this case, cylindrical geometry can be used for the description of the rod expansion process. The movement takes place only in the radial direction. The magnetic field has an azimuthal component  $H$  and the electric field has only a component  $E$  along the rod axis. We suppose the wavelength  $\lambda \simeq c/\omega$  according to the typical field frequency  $\omega$  is larger than the circuit dimension ( $c$  is the velocity of light). The hydrodynamical part of the system of equations has the following form:

$$\frac{\partial \rho}{\partial t} + \frac{1}{r} \frac{\partial}{\partial r} (\rho r v) = 0 \quad (1)$$

$$\frac{\partial v}{\partial t} + v \frac{\partial v}{\partial r} = -\frac{1}{\rho} \frac{\partial P}{\partial r} - \frac{jH}{c\rho} \quad (2)$$

$$\frac{\partial s}{\partial t} + v \frac{\partial s}{\partial r} = \frac{j\mathfrak{E}}{\rho T} \quad (3)$$

Here  $r$  is the radius vector in cylindrical coordinates,  $v$  is the velocity,  $s$  is the specific entropy,  $P$  is the pressure, and  $\rho$  is the mass density. The intensity of the electric field  $\mathfrak{E}$  measured by an observer which is in rest relative to a particular region of substance is given by  $\mathfrak{E} = E + (1/c) vH$ . The current density  $j$  and the intensity of the electric field  $\mathfrak{E}$  are related by Ohm's law  $j = \sigma\mathfrak{E}$ , where  $\sigma$  is the conductivity.

Maxwell's equations in this case are expressed as

$$\frac{\partial E}{\partial r} = \frac{1}{c} \frac{\partial H}{\partial t} \quad (4)$$

$$\frac{1}{r} \frac{\partial}{\partial r} (rH) = \frac{4\pi}{c} j \quad (5)$$

We assumed that the contribution of displacement current is relatively small.

The viscosity can be neglected, so far as we do not consider the structure of shock waves. Also, thermal conductivity has no importance in the studied process [5].

Boundary conditions for the intensity of magnetic field  $H$  are as follows:  $H(0, t) = 0$ ,  $H(a, t) = 2I/ca$ , where  $I$  is the total current through the sample. The equation for  $I$  can be written in the following way:

$$\frac{L_0 + L_s}{c^2} \frac{dI}{dt} + \frac{I}{2c^2} \frac{dL_c}{dt} + E_{sr}l + U_c = 0 \quad (6)$$

where  $L_0$  and  $L_s$  are the inductance of the discharge circuit and the sample, respectively,  $E_{sr}$  is the intensity of the electric field on the surface of the rod, and  $U_c = U_0 + C_0^{-1} \int_0^t I(t) dt$  is the capacitor bank voltage ( $U_0$  is the charge voltage and  $C_0$  is the capacity). The rod inductance has a magnitude of the order of  $L_s \simeq 2l \ln(l/a)$ .

We considered a discharge through the sample in air under normal conditions. The diamond synthesis pressure is much higher than the carbon vapor pressure at 2000–4000 K. Hence this pressure has not been taken into account.

The most suitable carbon equation of state for our purpose [6] was obtained on the basis of experimental data concerning isentropic expansion and shock loading of matter. This equation of state is presented as a dependence of pressure  $P$  and specific energy  $\mathcal{E}$  versus density,  $\rho$ , and temperature,  $T$ :

$$P = P_x(\rho) + \Gamma(\rho) \rho C_v (T - T_0) \quad (7)$$

$$\mathcal{E} = \mathcal{E}_x(\rho) + C_v (T - T_0) \quad (8)$$

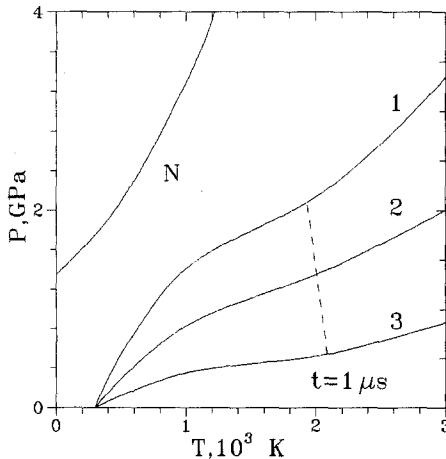
where  $\Gamma$  denotes the Grüneisen coefficient and  $C_v$  the specific heat ( $T_0 = 300$  K). As long as the characteristic diamond synthesis temperature is relatively low, electronic components in Eqs. (7) and (8) are negligible. These components become considerable at temperatures of about  $10^4$  K and higher.

### 3. NUMERICAL MODELING RESULTS

For the numerical solution of Eqs. (1)–(3), Godunov's method was used. Maxwell's equations were solved by means of the finite difference method [7].

The calculations were made for the circuit parameters and geometric size of the sample as follows:  $C_0 = 216 \mu\text{F}$ ,  $L_0 = 0.11 \mu\text{H}$ ,  $l = 3 \text{ cm}$ , and  $a_0 = 0.15 \text{ cm}$ . In Fig. 2 (on the  $P, T$  plane) the evolution of the carbon state over area of the sample is given. To be exact, in this figure the curves corresponding to the three particular regions of sample are given. These regions have Lagrange coordinates of, respectively,  $m = 0, \frac{1}{3}$ , and  $\frac{2}{3}$ , where  $m = \int_0^r \rho r dr / \int_0^a \rho r dr$ . As one can see, for this regime the synthesis conditions are not achieved. The modeling results have indicated that synthesis conditions cannot be achieved for graphite samples by means of the electrical current impulses produced by such electrical circuit; the temperature rises more quickly in comparison with the pressure rise to achieve the diamond stable domain (see Fig. 2).

We considered also graphite samples contained in the tube. In Fig. 3, the evolution of the graphite state for such a regime is given. The circuit parameters and the sample size were just the same as for the regime



**Fig. 2.** Path of a particular region of carbon on the  $P, T$  plane during the electrical explosion process for a graphite sample. Curves 1, 2, and 3 correspond to particular regions having Lagrange coordinates of  $0, \frac{1}{3}$ , and  $\frac{2}{3}$ , respectively. The dashed line represents the state of the sample over its area at  $t = 1 \mu\text{s}$ .

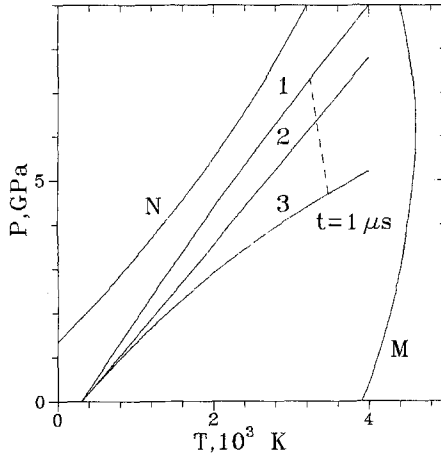


Fig. 3. Graphite sample contained in a massive tube. M is the melting line of graphite (see the legend to Fig. 2).

presented in Fig. 2. The tube had an inner radius coinciding with the rod radius and the outside radius was equal to 0.8 cm. The conductance of the tube was assumed to be zero. As illustrated by calculating the results in this case, the pressure was higher, but the diamond synthesis domain was not achieved. Hence the graphite conductivity is too low. The temperature rises too quickly to realize the synthesis conditions. The path of particular regions of graphite on the  $P, T$  plane crosses the melting line.

We carried out modeling for samples made of a composite material having a higher conductance than graphite. This material is a mixture of metal and graphite particles. We assumed that the porosity of the material is negligible and graphite particles have the effective size  $r_p \leq (\chi t_T / \rho C_V)^{1/2}$ , where  $\chi$  is the thermal conductivity of graphite and  $t_T$  is the temperature rise time.

For such a material the specific energy can be presented by

$$\mathcal{E}(\rho, T) = x\mathcal{E}_g(\rho_g, T) + (1-x)\mathcal{E}_m(\rho_m, T) \quad (9)$$

where  $x$  is the mass fraction occupied by graphite. Subscripts g and m refer to graphite and metal, respectively. The equation of state of the metal was considered to be of the form of Eqs. (7) and (8). Equations (7)–(9) and

$$\rho = x\rho_g + (1-x)\rho_m, \quad P_g(\rho_g, T) = P_m(\rho_m, T) \quad (10)$$

are the set of equations of state for the composite material.

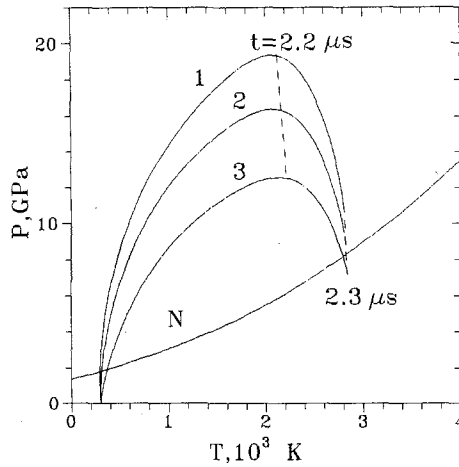


Fig. 4. Composite sample for the regime with the current cutting off (see the legend to Fig. 2).

The conductivity of such a material was described by means of the effective medium formula [8]. Conductivities of the metal and graphite were obtained from the fit to the experimental data given in the literature [9, 10].

In Fig. 4 the path of a particular region of carbon on the  $P, T$  plane is shown for a composite sample. The metal component of the material was aluminium, the volume fraction of the metal was 60%, and the length of the rod was 3 cm and its diameter 0.15 cm. As one can see, for this regime

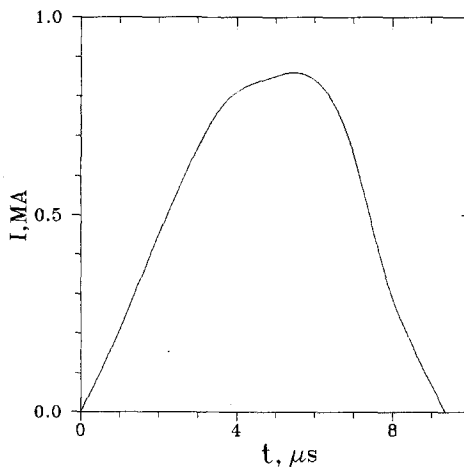


Fig. 5. Current through the composite sample.

diamond synthesis conditions are achieved. At time  $t = 2.2 \mu\text{s}$ , the current through the sample was cut off. In this way we investigated the possibility of carbon state control to reduce diamond loss at high pressures.

#### 4. EXPERIMENTAL DATA

At our institute, the first preliminary experiments of diamond production by capacitor bank discharge were performed with a graphite-containing composite sample. In Fig. 5 currents through the sample are shown for a regime with parameters as follows:  $C_0 = 144 \mu\text{F}$ ,  $L_0 = 0.11 \mu\text{H}$ ,  $U_0 = 35 \text{ kV}$ ,  $a_0 = 0.175 \text{ cm}$ , and  $l = 1 \text{ cm}$ . The sample was made of a composite material containing 9%, by mass, of graphite, the metal component was copper, and the electrical resistivity of the material was  $25 \mu\Omega \cdot \text{cm}$ . X-ray examination indicated that the product of this synthesis was diamond having an average crystallite size in the range of  $0.1\text{--}0.2 \mu\text{m}$ . In our experiments hexagonal and cubic diamond was obtained. In the regime presented in Fig. 5 cubic diamond was not detected. The yield of diamond converted from graphite for this regime was about 10%.

#### 5. CONCLUSIONS

Numerical modeling results and experimental data on diamond synthesis by means of capacitor bank discharge showed that diamond synthesis conditions can be created by the use of a composite material having a metallic conductivity. Moreover, it is necessary for the current to be not less than 1 MA. The diamonds synthesized by this method differ from diamonds obtained by shock synthesis. In this case, the average size of crystallites is in the range from 0.1 to  $0.2 \mu\text{m}$ .

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