Shock loading of graphite between water layers: Numerical experiments

L V Shurshalov¹, A A Charakhch’yan¹ and K V Khishchenko²
¹ Dorodnicyn Computing Centre, Federal Research Center “Computer Science and Control” of the Russian Academy of Sciences, Vavilova 40, Moscow 119333, Russia
² Joint Institute for High Temperatures of the Russian Academy of Sciences, Izhorskaya 13 Bldg 2, Moscow 125412, Russia
E-mail: lshur@ccas.ru

Abstract. A series of numerical experiments on shock loading of graphite between water layers is realized. A simple model of the phase transition of graphite to diamond is formulated. The general scheme of the computational experiment is based on mechanical and thermal interactions of different substances (graphite, diamond, water) subjected to impact by a massive steel flyer in a cylindrical channel. The process of graphite-to-diamond transformation is traced out. The important problem of retaining the formed diamond sample and some favorable conditions to solve this question are discussed.

1. Introduction
This work is devoted to some numerical experiments, in which graphite is compressed in shock waves and undergoes the phase transition to diamond. The aim is to find perspective approaches as to formation of diamond from graphite and also to retaining the diamond phase after the pressure and temperature release to normal conditions. The synthetic diamonds are rather successfully obtained in quasi static compression and heating processes [1]. But dynamically in a short time scale, the synthesis of diamonds is still on demand. Only ultra small diamonds can be obtained by dynamic compression. Experiments show [2–4] that graphite being dynamically compressed to 20–30 GPa may convert to diamond. But after pressure drops to normal value, the residual temperature is left so high that it causes the diamond almost completely reverts to the graphite phase. So, one of the main problem in dynamic experiments is to prevent the formed diamond returning to the graphite phase. Some special measures must be taken to cool the diamond almost as quick as the pressure drops. Some aspects of this problem are considered in this paper by means of computations.

2. The scheme of the computational experiment
In figure 1, the schematic picture of the one-dimensional numerical experiment is shown. We suppose that the process happens in a cylindrical channel with absolutely rigid walls. A graphite sample in the form of a tablet with the thickness \( d \) is placed in the channel. On the both sides of the tablet, two layers of water with the same thickness \( d \) are placed. A massive steel plug of the rather large thickness of 30.5 cm is neighboring the right water layer. The plug may move...
Fe FeCH O₂ H O₂ 0 z

Figure 1. Schema of the numerical experiment.

along the channel under the action of the arising flow. The left water layer is impacted by a steel flyer that has the thickness of 20.5 cm and the velocity of 1.3 km/s.

The aim of the numerical experiment is to study such a configuration and to trace out phase transitions of graphite to diamond and possibly later of diamond to graphite. It is not a simple problem to be solved to get the first phase transition and then prevent the second one. We hope that some results of our investigation will contribute to the solution of this problem and will help to obtain synthetic diamonds of noticeable size in physical dynamic experiments.

The equations describing the flow are taken in the following form:

\[
\begin{align*}
\frac{\partial \rho}{\partial t} + w \frac{\partial \rho}{\partial z} + \rho \frac{\partial w}{\partial z} &= 0, \\
\frac{\partial w}{\partial t} + w \frac{\partial w}{\partial z} + \frac{1}{\rho} \frac{\partial P}{\partial z} &= 0, \\
\frac{\partial}{\partial t} \left( \rho \frac{e}{2} + \frac{w^2}{2} \right) + \frac{\partial}{\partial z} \left[ w \left( \rho \frac{e}{2} + \frac{w^2}{2} + P \right) - \kappa \frac{\partial T}{\partial z} \right] &= 0,
\end{align*}
\]

where \( t \) is the time, \( z \) and \( w \) are the coordinate and the velocity along the channel axis, \( \rho \) is the density, \( P \) is the pressure, \( e(P, \rho) \) is the specific internal energy, \( T \) is the temperature, \( \kappa \) is the heat conductivity coefficient.

The Godunov method [5] was used to calculate these equations. The initial values of the pressure \( P_0 = 0.1 \) MPa and temperature \( T_0 = 288 \) K are supposed to correspond to the normal conditions at the sea level. The initial values of the substances density are denoted as \( \rho_0 \).

3. Equations of state
The two-term equation of state [5] is used for the thermodynamic description of the substances in question. The caloric and thermal parts of the equation of state were taken in the following form:

\[
\begin{align*}
e &= \frac{(P + \gamma P^*)}{(\gamma - 1)\rho} - \frac{\gamma P^*/(\gamma - 1)\rho}{\gamma - 1}, \\
P &= (\gamma - 1)\gamma P^* + P^*[\rho/\rho^*]^\gamma - 1, \\
P^* &= \rho^* C_0^2/\gamma,
\end{align*}
\]

where \( \gamma, P^*, \rho^*, c_v \) and \( C_0 \) are the constants having the meaning of the adiabatic index, the characteristic pressure for a given substance, the density at which the cold part of pressure is zero, the specific heat capacity and the characteristic sound velocity corresponding to the normal pressure and the density equal to \( \rho^* \).

The choice of these constants was discussed in detail previously [6, 7]. Now we only list their values used in the calculation (table 1).

It is commonly admitted that the equation of state (2) rather well describes thermodynamic properties of metals, solids and liquids under high pressures. In addition it correctly reflects the important feature of solids and liquids in the process of their unloading from great values of pressure and temperature to normal ones. Namely, metals and other solids like diamond and graphite retain high residual temperatures after unloading while liquids undergo considerable expansion and strong lowering of the temperature.

At this study, we limit ourselves by constant heat conduction coefficients \( \kappa \) taking their characteristic typical values (see table 1).
Table 1. Thermophysical constants of the materials in question.

| Material | $\rho_0$, g/cm$^3$ | $\rho^*$, g/cm$^3$ | $\gamma$ | $C_0$, m/s | $c_v$, J/kg/K | $\kappa$, W/m/K |
|----------|-------------------|-------------------|---------|-----------|-------------|-------------|
| Graphite | 2.26              | 2.266744043       | 1.24    | 3950      | 674         | 200         |
| Diamond  | 3.5               | 3.50639456        | 2.15    | 11270     | 700         | 2000        |
| Water    | 1.0               | 1.3223454         | 4.3     | 4043.8578 | 3700        | 0.6         |
| Steel    | 7.87              | 7.9561481         | 3.0     | 5000      | 470         | 50          |

Figure 2. Phase diagram of carbon.

4. Phase transitions modeling

Different models of carbon phase transitions are known [3,8–13]. In the present work, we suggest a very simple engineering approach to phase transitions of graphite to diamond based on the experimental $P-T$ diagram for carbon [1] that is shown in figure 2.

The practically right line marked in figure 2 as $Ph_1$ is the equilibrium boundary between the graphite and diamond phases. Since the transformation process from graphite to diamond is not instantaneous but demands some time, then crossing this line by the trajectory of $P-T$ parameters of the carbon will not lead to immediate formation of diamond. This process may only start at this line. It will finish only after the $P-T$ trajectory crossing the considerably higher line, which we have indicated as $Ph_2$. This line may be chosen differently. For example, it may be taken like the line BFG in figure 2 limiting the zone where, as some experiments show, graphite transforms into the cubic diamond in less than 1 $\mu$s. Some other experiments [2–4] demonstrate that rather short transformation of graphite to diamond under dynamic compression happens, if the shock wave pressure exceeds 20–30 GPa.

Unlike the above-mentioned BFG line, the transition line $Ph_2$ allows for instant transition of graphite into diamond in the region of variables ($P, T$), where the real transition can occur in time interval longer than 1 $\mu$s. However, our choice of the transition line $Ph_2$ seems acceptable for the problem considered below, as the action of the high pressure on the carbon sample lasts by several tens of microseconds.

In an analogous manner the reverse transition from diamond to graphite may be considered [6]. But it was not necessary in our present case. As shown in experiments [14,15], diamond
Figure 3. (On the left) Displacements of carbon and water boundaries for $d = 5$ mm.

Figure 4. (On the right) Maximum pressure in the carbon sample for $d = 5$ mm.

samples in a vacuum are not graphitized practically at temperatures less than 1900 K. All the more, it must be valid so at higher pressures. In our present numerical experiment the diamond temperature never exceeded 1000 K.

5. Results
We begin with the above mentioned variant of experiment with $d = 5$ mm, i.e. with the initial thickness of the graphite tablet being equal to the thicknesses of the water layers on each side of the tablet. The rest parameters (listed in section 2) were chosen after numerous calculations because of some useful features of the variant.

First of all, the large thicknesses of the plug and the flyer prevent early appearance of strong unloading waves till times $t$ of 100–120 $\mu$s. Such waves coming from either side of the sample having considerable negative (tensile) pressures could destroy the materials and the flow.

Another useful feature is the transition of graphite to diamond at $t \approx 13$ $\mu$s in the whole of its volume. During the next 50 $\mu$s, the diamond is under the condition corresponding to the line $Ph_2$, i.e. $P \approx 30$ GPa. And after that, till 120 $\mu$s, it still retains as diamond. That is rather long time. Unloading of the sample continues very smoothly almost till the normal pressure comes and till unloading waves with destroying negative pressures arrive.

The third attractive feature is practically uniform pressure and density distributions in the sample during the all major stage of the experiment.

Now we will illustrate all these and other features of the flow. In figure 3, the displacements with time $t$ of the sample boundaries (solid lines) and the two outer boundaries of the adjacent water layers (dashed lines) are shown. Due to mobility of the plug, the flow configuration is moved as a whole to $z \approx 6$ cm. After 80–90 $\mu$s, with decreasing pressure, the water layers around the sample begin expanding with considerable decrease of their temperature.

The maximum pressure history in the sample is presented in figure 4. The initial short stage relates the shock-wave action by the flyer and by a series of reflected from the plug and the flyer shock waves resulted in the maximum pressure reaching approximately 30 GPa. This value of the pressure retains of about 50 $\mu$s. After 15 $\mu$s, the pressure is homogeneous in space and only begins to diminish its value in 50 $\mu$s. The pressure distributions within the sample and water layers are shown as a function of the Lagrangian coordinate $L$ for some time moments in figure 5. The boundaries between the sample and the water layers correspond to $L = 20$ and 40.
Figure 5. (On the left) Pressure distributions in the carbon and water layers for \( d = 5 \) mm.

Figure 6. (On the right) Maximum temperature in the carbon (solid line) and adjacent water layers (dashed curves) for \( d = 5 \) mm.

In figure 6, the maximum temperature in the sample (solid line) and in the two water layers (dashed curves) are shown as functions of time. In this example, the temperature in the diamond sample reaches the value of 800 K, while the temperatures of water are considerably higher and reach 1300–1500 K. As it is seen, the sample temperature for the considered time interval of 120 \( \mu s \) changes rather slowly and mainly within 200 K. The water layers after 60 \( \mu s \) begin rapid cooling. Their temperature becomes much lower than the temperature of the sample.

The temperature and density distributions along the Lagrangian coordinate \( L \) for three time moments in the sample and the two water layers are shown in figure 7. The density does
practically not depend on \( L \) like the pressure (see figure 5) with only exception that it breaks at the boundaries of the sample and the water layers. The temperatures distributions are less homogeneous. The heat conduction slightly smears the temperatures near the boundaries of the sample with water.

The distributions of the velocity within the sample and also within the water layers turn out to be practically linear. This allows constructing an analytical solution to the problem using the well-known family of solutions with the linear velocity profile described in [16], in particular, the part of the mentioned family with constant in space thermodynamic functions [17].

Though the temperature of the formed diamond in the considered example is rather low, the important question is left how to quickly cool the formed diamond to normal temperature at those 100–120 \( \mu \)s before the spall release wave arrives. The results show that, for such a thick sample as used with \( d = 5 \) mm, there is not enough time for the heat conduction to cool the sample even though that the surrounding water temperature drops down very rapidly.

So, we have decided to carry out an additional investigation to see at what thickness of the sample its temperature would decrease as quickly as the temperature of the surrounding water.

We start with the example of \( d = 1 \) mm. All the rest parameters of the numerical experiment are not changed.

In figure 8, we present the results analogous to those given in figure 6 but with some addition. The maximum temperatures of the water layers are drawn here by the two dotted curves. They behave in the same manner like in figure 6. The maximum temperature of the sample is shown by the solid line. We add the dashed line showing the minimum temperature of the sample. It is interesting to see the difference between these two temperatures because it shows the homogeneity of the temperature within the sample. In this example, initially, this difference is considerable. The temperature near the boundaries with water is much higher because of the higher temperature of water. The heat conductivity of diamond (formed in this case at \( t \approx 2.5 \) \( \mu \)s), however great it is, makes the temperature almost homogeneous only at \( t = 60 \) \( \mu \)s. But later, the homogeneity is again disturbed due to diminishing of the flow pressure resulted in the rapid cooling of water and the corresponding cooling of the diamond sample near the boundaries with water. The central part of the diamond sample cannot be cooled in the same way rapidly. So, the difference between the maximum and the minimum temperatures again increases.

**Figure 8.** Maximum (solid lines) and minimum (dashed lines) temperatures in the carbon and maximum temperatures in the adjacent water layers (dotted lines) for \( d = 1 \) (on the left) and 0.2 mm (on the right; the initial stages at \( 0 \leq t \leq 0.5 \) \( \mu \)s are not shown).
This is well seen from the left-hand side of figure 9, where the temperature distributions within the diamond sample and the adjacent water layers are shown for some time moments along the Lagrangian coordinate $L$. Figure 9a corresponds to the stage of the sample heating. At $t = 60 \mu s$, the temperature in the sample is practically homogeneous. Figure 9b corresponds to the stage of the rapid water cooling. The diamond sample in spite of its high heat conduction cannot be in time with the water temperature in the whole of its volume even in this case of the rather small its thickness. Evidently, the diamond heat conduction cannot provide cooling of the 1-mm diamond sample in time with the cooling of water for such short time periods.

To find out the minimal thickness of the diamond, for which the heat conduction will provide homogeneous heating and cooling of the sample, we perform calculations of rather exotic example with $d = 0.2$ mm and the same other parameters of the numerical experiment. The results are shown in figures 8 and 9 (on the right-hand side).

One can see from the right-hand side of figure 8 that the difference between the maximum and the minimum temperatures of the diamond sample is practically absent with the exception of a very short initial time moments, when the first shock wave propagates from the left side of the sample to its right side thus initially creating the difference between the maximum and minimum temperatures. This difference is supported not long (while diamond is not formed) due to much lower heat conductivity of graphite. Moreover, the cooling of the diamond sample at later times follows the cooling of the surrounding water.
The same features but in more detail are illustrated by the right-hand side of figure 9 showing the temperature distributions in the sample and the adjacent water layers for the heating and the cooling stages of the process. At the former stage, the homogeneity of the diamond temperature is achieved very shortly and is very well retained. At the latter stage, the homogeneity of the diamond temperature is slightly disturbed due to more rapid cooling of the sample edges. The cooling of diamond proceeds somewhat slower than that of water but, on the whole, this process is very rapid and considerable.

Thus, rather small pieces of graphite may be effectively heated and cooled by the surrounding water layers. Evidently, the scale of the process may strongly influence the results. For greater scale, the heating and cooling durations will increase together with the sizes of the corresponding carbon samples.

6. Conclusions
The obtained results show the importance of rapid cooling to retain the carbon samples in the diamond phase. Water can be a suitable refrigerating medium for this purpose. Though it has very low heat conductivity, it possesses rather high heat capacity that allows even small quantities of water to take away considerable amount of heat. And it lowers its temperature very rapidly down to very low values, when the surrounding pressure diminishes. But the process demands some time. That is why the diamond samples with the thickness $d = 5$ mm and even $d = 1$ mm cannot be cooled to the normal temperature in 100 $\mu$s. Smaller diamond samples can be cooled quite effectively over such short periods.

That gives perspective to the consideration of shock loading experiments with the mixtures of water and graphite particles. Rather small graphite particles in surrounding water may be first heated and compressed by shock waves, undergo transition to the diamond phase, then exchange some heat with compressed and heated water. At the expansion stage, water begins rapidly cooling and the diamond particles may be cooling almost in time with it. The presence of water may be useful also at later times, when the spalling release waves arrive. They will cause the fracture of the mixture along the weakest lines. In this case, they will spall water but not the diamond particles.

Our calculations were carried out on the basis of a very simple two term equation of state. That may give some deviations of thermodynamic parameters from their real physical values. So, it is worth to repeat the calculations using more realistic though more complicated equations of state for graphite, diamond and water. Still we hope that our conclusions will be left valid after such reconsideration.

Acknowledgments
This work is financially supported by grants from the Russian Foundation for Basic Research (No. 14-08-00967) and the President of the Russian Federation (No. NSh-10174.2016.2), as well as program of the Presidium RAS (No. I.11P “Thermophysics of high energy densities”).

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