Cavitations synthesis of carbon nanostructures

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Abstract. Originally an idea of diamonds production by hydrodynamical cavitation was presented by academician E M Galimov. He supposed the possibility of nature diamonds formation at fast magma flowing in kimberlitic pipes during bubbles collapse. This hypothesis assumes a number of processes, which were not under consideration until now. It concerns cavitation under high pressure, growth and stability of the gas- and vapors bubbles, their evolution, and corresponding physical- and chemical processes inside. Experimental setup to reproduce the high pressure and temperature reaction centers by means of the cavitation following the above idea was created. A few crystalline nanocarbon forms were successfully recovered after treatment of benzene (C\textsubscript{6}H\textsubscript{6}).

1. Introduction

Mainly, nanodiamonds (ND) and other carbon nanostructures are produced by means of detonation of explosive containing carbon [1], [2] or by CVD [3], PVD [4] methods and laser ablation [5] now. Hydrodynamical cavitation at carbon contacting liquids [6], [7] provide alternative way, where a number of advantages are evident (control of impurities, defects structure, etc.). Additional interest to the cavitations concerns manipulation with the carbon nanotubes. Shock waves and jets, which are results of the bubbles collapsing, can deform effectively nanostructures providing possibility to investigate theirs physical- and mechanical properties [8]. So, hydrodynamical cavitation is unique process which strongly differs from acoustical cavitation (produced by sound wave with small amplitude in the liquid) concerning carbon nanostructures creation and control of their size and properties.

From the general point of view, the physics by cavitational bubbles collapsing and by shock-compression is very similar. But, the environment conditions, especially theirs that appropriate for the rapid cooling, are important as well. For example, detonation nanodiamonds production crucially depends on the synthesis condition and especially on the heat capacity of the cooling medium in the detonation chamber (water, air, CO\textsubscript{2}, etc.). The higher the cooling capacity, the larger the detonation nanodiamonds yield, which can reach 90%. Various measurements, including X-ray diffraction and high-resolution TEM [9] revealed that the size of the diamond grains in the soot is distributed around 5 nm. The purpose of this study is to investigate a new rapid cooling technique under shock compression during hydrodynamical cavitation and to clarify carbon behavior under special range of P-T conditions. A few crystalline nanocarbon forms were found in the samples recovered from the benzene after treatment at the proper experimental setup. The results of characterization for the produced nanocarbon forms by means of the transmission electron microscope (TEM) and Raman spectroscopy are reported.
2. Experimental setup
At GEOKHI RAS experimental setup was constructed in collaboration with Moscow Bauman Technical University, group of Prof. V N Skorobogatskiy, to argue the idea of academician E.M. Galimov. Schema of the experimental setup is shown in the figure 1.

![Experimental setup](image)

**Figure 1.** Experimental setup: two work cavities 2 and 3 are joined by Venturi tube; q1 and q2 are moving pistons; d-1, d-2, d-3 and d-4 are pressure sensors.

It includes the cavities (1) and (4), in which the ignition of the powder charges occurs and pistons q1 and q2 were moved. The cavities (2) and (3) and jet block accomplished in the form of the Venturi tube are filled with the working liquid (benzene). The profile of the Venturi tube in its critical section provides the decrease of pressure of flowing liquid lower than the pressure of its saturated vapors and its continuous flow in the diffuser part. The experimental installation operates in the following way: under action of pressure of the powder gases formed in the cavity 1 the piston q1 begins to move and drives the liquid from the cavity 2 into the cavity 3 through the Venturi tube. At that time the vapor bubbles are formed in the minimum section of the Venturi tube (the first stage of cavitations). These bubbles increase in their size and get into the cavity 3. The piston q3 moves in its extreme right position and pin out the cartridge primer, which initiate the powder cartridge in the cavity 4. Under pressure of the powder gases in the cavity 4 the piston q2 gets the impulse in the reverse direction that generate the shock wave in the cavity 3, which initiate the condition for the adiabatic collapse of the vapor bubbles and diamond producing.

Pressure measurements were made during experiments by means of number of pressure sensors d-1, d-2, d-3, d-4 at the cavities and Venturi tube. Pressure levels at benzene were at the interval from 80 MPa to 140 MPa, pressure drop at the cavity 3 (until initiation of the powder cartridge in the cavity 4) was from 0.002 MPa to 0.1 MPa, pistons velocities were about 2 m/sec. In some experiments, temperature sensor was installed instead pressure sensor at the cavity 3. Its value demonstrate that the initial temperature of benzene was not remarkable changed during the flowing, so the process was considered as isothermal in modeling.

After tuning of the setup experimental parameters, the second phase of the bubbles collapse was produced as planned. Namely, spherical-symmetric adiabatic bubbles collapse in the cavity 3 under proper external pressure jump.

3. Analysis of results
There are reliably registered sparkling grains of the nanodiamonds from 5 to 20 nanometers in size and aggregates of different forms of diamonds and graphite till 1-5 micrometers in size, see figure 3. Investigation of grains observed under transmission electron microscope was carried out by JEOL JEM100-C11 by Prof. A S Aronin (ISSP RAS, Chernogolovka). Renishaw InVia Reflex Spectrometer system for Raman spectral analysis using visible excitation at 785 nm was prepared by Dr. A Eliseev, Chemistry Department, MSU, see figure 4.
Raman spectroscopy is particularly well suited to molecular morphology characterization of carbon materials. Every band in the Raman spectrum corresponds directly to a specific vibrational frequency of a bond within the molecule. The vibrational frequency and hence the position of the Raman band is very sensitive to the orientation of the bands and weight of the atoms at either end of the bond. So, when we compare the Raman spectra of two carbon allotropes – diamond and graphite – we can easily distinguish the two materials by their Raman spectrum even though both are composed entirely of C-C bonds. The graphite spectrum has several bands in the spectrum and the main band has shifted from 1332 cm$^{-1}$ in cubic diamond to 1582 cm$^{-1}$ in graphite [11]. The reason for this is that graphite is composed of sp2 bonded carbon in planar sheets in which the bond energy of the sp2 bonds is higher than the sp3 bonds of diamond. The higher energy of the sp2 bonds in graphite pushes the vibrational frequency of the bonds and hence the frequency of the band in the Raman spectrum to higher frequency. The presence of additional bands in the graphite spectrum indicate that there are some carbon bonds with different bond energies in the graphite sample and this is in fact the case, as graphite is not quite as uniform in structure as diamond.

Another good example to show the remarkable sensitivity of Raman to molecular morphology is to compare the Raman spectra of produced nanocrystalline diamonds with that of industrial nanodiamond grains (see figure 2 and figure 4) recovered from the shock-compressed graphite (SCG) at 60-70 GPa, which present intermediate and metastable phase on a way to cubic diamond. The small crystal size of nanocrystalline diamond results in a finite-size effect in which the lattice is somewhat distorted. This is manifested in the Raman spectrum by a slightly downshifted tetrahedral sp3 band. The additional band at 1340 cm$^{-1}$ and the shoulders on the 1350 cm$^{-1}$ and tetrahedral sp3 band are also indicative of sp2 bonded carbon that represents surface defect modes, which would be insignificant in larger diamond crystals.

Finally, Raman can reveal a lot of information about more complex carbon structures. So, fullerenes are essentially hollow carbon shells of various sizes. The most well known of these is a 60-carbon unit called Buckminster fullerene or C60. There are many other fullerenes, from a few to many hundreds of carbon atoms. The main feature in the C60 spectrum is a relatively sharp line at around 1462 cm$^{-1}$, known as the pentagonal pinch mode. This tells us several things. Firstly, it tells us that...
C60 is composed of sp2 bonded carbon. The sharpness of the band also tells us that the bonds are for the most part very uniform in nature. In fact, the carbon atoms in C60 are equivalent and indistinguishable. In contrast, the spectrum of the produced nanocarbon forms (see in figure 4) is littered with numerous bands. This is due to a reduction in molecular symmetry which results in more Raman bands being active. So, we can suppose complex fullerene-forms or nanosized crystalline graphite as resulting nanocarbon forms after cavitational bubbles collapsing.

Figure 4. Raman spectrum of different samples: [1] – ND and shock-compressed graphite mixture; [2] – nanocarbon forms after hydrodynamical cavitation at benzene.

4. Conclusions
The experimental setup description and the results of the experiments with the hydrodynamical cavitation at benzene are presented. Grains of diamonds in size of 5-20 nm and aggregates of different carbon nanostructures are obtained. The transmission electron microscopy and Raman spectroscopy methods were used to compare produced nanocarbon forms with industrial nanodiamond grains from the shock-compressed graphite. These results support the idea academician E M Galimov that the thermodynamic conditions inside of cavitational bubbles during collapse are appropriate for the diamond phase formation and provide new alternative method of carbon nanostructures synthesis.

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