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Structure of detonation nanodiamonds

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Nanoparticles of diamond were formed from detonations, and density and other measurements indicate they are hollow. The most likely explanation is that they condensed from liquid carbon which is less dense than diamond.

In contrast to other synthetic diamonds, the particles of superdispersed diamonds are characterised by a round shape with diameter 4 nm.[1,2] Weathers and Bassett[3] described the formation of spherical diamond particles from 5 to 1000 nm in diameter in the course of melting graphite and diamond at high pressures. The samples of dispersed diamonds as a mixture with sodium chloride were placed between diamond anvils and heated by laser radiation. Round-shaped particles up to 100 nm in size were formed by detonation of a mixture of carbon with cyclotrimethylenetrinitramine[4] or by pulse heating of graphite particles mixed with a metal.[5] The density of superdispersed diamonds is about 3.1–3.3 g cm^{-3},[6–9] whereas natural and synthetic diamonds have densities approximately equal to a theoretical value of 3.515 g cm^{-3}. Therefore, we examined the structure of superdispersed diamonds.

According to our experimental data, the X-ray powder diffraction pattern of superdispersed diamonds exhibits only five reflections with a changed distribution of relative intensities: (111) 85.0% {44}, (220) 14.0% {22}, (113) 0.5% {18}, (400) 0.3% {4}, (331) 0.2% {12} (the relative values of a share of reflections for a standard diamond sample on ASTM Index 6-675 are given in braces). The crystal lattice parameter is 0.3562±0.0004 nm, whereas it is equal to 0.3567 nm for natural diamond. These data suggest that the theoretical density of the nanodiamonds is 3.527 g cm^{-3}. However, the helium pycnometric density is as low as 3.05–3.10 g cm^{-3}. The heating of superdispersed diamonds in inert atmospheres for 2 h affected their density (Table 1). The maximum density of nanodiamonds (3.21 g cm^{-3}) was achieved by heating in an argon atmosphere up to 1073 K (similar values were reported[6–9] for superdispersed diamonds after different treatments). Note that the theoretical density[10] of liquid carbon is 3.2191 g cm^{-3}.

A difference between the theoretical (X-ray) and experimental (helium pycnometry) densities can be explained, if we suppose that diamond was formed through a liquid phase in all of the above explosive processes. Melted diamond has a greater molar volume than that of the equilibrium solid phase.[11,12] Because of this, cavities will be formed in the crystallization of melted diamond particles upon external cooling (as is the case, for example, in the crystallization of liquid aluminum oxide on the combustion of aluminum particles[13]). It is reasonable to believe that hollow spheres will be formed in rapid crystallization of liquid particles of diamond at high temperature and pressure gradients.

Table 1 Pycnometric densities of superdispersed diamonds after heating in inert atmospheres.

Temperature/K	Pycnometric density/g cm^{-3} Atmosphere		
	Ar	H_2	CO_2
473	3.05	3.07	3.09
573	2.99	3.02	3.11
673	3.10	3.11	3.03
773	3.00	3.05	3.00
873	3.02	3.07	3.03
973	3.03	3.11	3.03
1073	3.21	3.15	2.99
1173	3.08	3.06	3.02
1273	3.09	3.03	3.09

To evaluate the sizes of these cavities, we used helium pycnometric density data. This estimation is rough because of the experimental error (±0.001 g cm^{-3}) and the presence of oxidised carbon groups at the surface of superdispersed diamonds. Let us assume that this distinction is caused by the presence of spherical cavities in superdispersed diamond particles 4 nm in size (note that the density of superdispersed diamonds is 3.21 g cm^{-3} and the density of natural diamond is 3.515 g cm^{-3}). Then, the volume of cavities was calculated to be $1 - 3.21/3.515 = 0.087$ or 8.7%. For a particle 4 nm in diameter (volume of 33.493 nm^3), the volume of a cavity is 2.913 nm^3, which corresponds to a sphere 1.77 nm in diameter. Similar calculations based on the X-ray density of superdispersed diamonds (3.527 g cm^{-3}) gave the diameter of an internal sphere equal to 1.79 nm. Thus, the average wall thickness is 1.10 nm, which is somewhat longer than seven C–C bond lengths (0.154 nm).

It is well known that the maximum particle size of superdispersed diamonds prepared by benzotrifuroxane ($C_6N_6O_6$) detonation is 31 nm.[14] In this case, the diameter of an inner sphere and the wall thickness were calculated to be 13.74 and 8.7 nm, respectively; the latter value corresponds to 56 C–C bond lengths (for the pycnometric density of superdispersed diamonds 3.21 g cm^{-3}). Thus, we may believe that, as distinct from fullerenes, diamond spheres formed as a result of solidification exhibit variable structure.

The following characteristic properties of superdispersed diamonds can be explained by the presence of these internal cavities:

(1) The presence of only five reflections with a changed distribution of relative intensities in the X-ray diffraction patterns of superdispersed diamonds.

(2) The absence of high-order reflections from the X-ray diffraction patterns.[15]

(3) The apparent presence of a high volumetric fraction of an amorphous phase of diamond in superdispersed diamonds (up to 70%)[6] (the part of a sphere through which X-rays pass perpendicularly to the surface appears as a phase amorphous to X-rays, and the part through which radiation passes at a tangent to the surface, as a crystalline phase).

(4) A lower heat conductivity of composite materials based on superdispersed diamonds as compared with materials containing the same mass fraction of synthetic diamonds of static synthesis.[16]

This can also explain unsuccessful attempts to obtain samples of superdispersed diamonds of a higher density by removal of nondiamond carbon species from the surface of superdispersed diamonds *via* gradual oxidation of carbon[9] and a constant density of superdispersed diamonds (3.05 g cm^{-3}) after shock-wave sintering,[17] as well as the explosion of such diamonds after laser irradiation[18] (statically synthesised diamonds did not explode under these conditions).

In the ^{13}C NMR spectra, the chemical shift of superdispersed diamonds is 34.5 ppm,[15] whereas the corresponding values for diamonds of static synthesis and natural diamonds are 40 and 50 ppm, respectively.[19] Thus, superdispersed diamonds exhibit a difference from other diamond species.

It may be expected that cavities will be present in diamond particles prepared through a liquid phase of carbon by other methods such as detonation of carbon with cyclotrimethylenetrinitramine (in this case, the density was 3.15–3.25 g cm^{-3})[20] and pulse heating of carbon mixtures with a metal.[5] It is likely that in experiments[21] on laser melting of diamond particles under conditions of a sharp decrease in the pressure and temperature (as is the case in detonation methods) hollow diamond particles rather than continuous fullerene structures 200 nm in size may be formed. Probably, diamonds formed in space explosions will also exhibit such a hollow structure.[22]

It may also be expected that the density of melted diamond will be 3.21–3.25 g cm^{-3}. The lower density of the majority of superdispersed diamond samples can be explained by an additional contribution from dissolved gases to the volume of a formed cavity and by a fractal structure resulting from closed pores which were formed on the consolidation of separate liquid carbon particles. The volume of closed cavities can be estimated from the following relationship between the specific volumes of solid diamond and liquid carbon phases:

$$1/\rho = 1/\rho_1 + V_c,$$

where ρ and ρ_1 are the densities of superdispersed diamonds and a liquid carbon phase, which are equal to 3.05 and 3.22 g cm^{-3}, respectively, and V_c is the volume of closed cavities. Hence, it follows that $V_c = 1.7\times10^{-5}$ m^3 kg^{-1}.

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