DETONATION NANODIAMONDS: TECHNOLOGY, PROPERTIES AND APPLICATIONS

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Summary
The chapter discusses specifics in the technology of synthesis, the structure, main properties and applications of detonation nanodiamonds produced in explosion from carbon of the explosive. Various models of the structure of a detonation nanodiamond particle, methods employed in studies of the particle structure, and the potential inherent in particle surface modification are assessed. The physical and chemical properties of detonation nanodiamonds are briefly described. A short account is given of the history of discovery of the detonation method of nanodiamond synthesis and of the progress in the technology of their production. A glossary of the main terms used is provided. The main publications bearing on the technology, properties and applications of detonation nanodiamonds are listed.

1. Introduction
Diamond, a material unique in its remarkable beauty, hardness and chemical resistance, has been known from times immemorial. For hundreds of years, Mankind has been using natural diamonds; but it is only starting from the mid-1950s that one has begun industrial-scale synthesis of diamonds from graphite in the presence of metal catalysts in chambers capable of resisting high pressures, on the order of tens of thousands of atmospheres, and temperatures of about fifteen hundred degrees.

Annual world output of such synthetic (artificial) diamonds ranging in size from a few microns to hundreds of microns, the so-called diamond micropowder, amounts to hundreds of thousands of carats.

In the present time, however, when modern technologies are progressing steadily from dimensions measured in micrometers to the realm of nanoscale objects, we are witnessing a rising demand in diamonds of the corresponding sizes. Such nanodiamonds prepared by the detonation method (the so-called detonation nanodiamonds, DND), were first synthesized in the USSR, and their industrial-scale production was started in the late-1980s in Russia. The detonation or explosion method rests essentially on an attractive idea of using a shock wave to achieve the necessary high pressures and use the carbon of the explosive itself as a starting material to produce crystalline diamond. The short time of the explosion determined the small size of the diamond crystallites, only a few billionths of a meter; indeed, the size of a detonation diamond crystallite amounts typically to 3-5 nm.

Understandably, research in the area of the so-called detonation synthesis had been carried out for some time under the cloak of secrecy. Moreover, this method of preparation of nanodiamonds from the carbon of explosives was invented in the USSR independently and more than one time by different research groups (see the relevant historical note below).

Starting from 1988, the year of publication of the subsequently widely quoted papers on detonation diamonds in Russia and the USA, researchers have passed a long path indeed, from basic scientific studies covering the technology of production and characterization of DND to their industrial application.

Viewed from the standpoint of basic science, the interest in detonation nanodiamonds stemmed from their belonging to the family of novel nanocarbon materials discovered at the end of the last century, more specifically, the fullerenes, the onion-like carbon and nanographite. It was demonstrated that when treated in a specific heating regime nanodiamonds undergo restructuring to form carbon spheres enclosed into one another which resemble an onion or a multilayer fullerene. This onion-like carbon can, in its turn, transform again to a nanodiamond under electron beam impact. In addition to an attractive possibility of studying structural transformations at the nanolevel, a not less intriguing finding was a discovery of nanodiamonds in meteorites and a truly remarkable observation of an extremely narrow size distribution of nanodiamond crystallites peaking around 4 nm.

These discoveries alone would have been enough to spur the interest in nanodiamonds in the area of basic science, but it is the prospect of using nanodiamonds in industry that
underlay in the past and continues to account presently for the growing fascination in studying their properties.

The studies undertaken in the recent years have revealed that nanodiamonds can be employed to advantage as novel nanosized building blocks in developing nanocomposite materials, coatings that are unique in mechanical properties, nanoelectronic devices, selective adsorbents and catalysts, specific objects for use in medicine and biology.

Application of nanodiamonds opens a way to substantial improvement of the characteristics of abrasive and polishing compositions, lubricants, abrasive tools, polymer compositions, resins and rubbers, magnetic recording systems, and provides a possibility of growing diamond films on a variety of substrates.

Real progress in the technology of production of detonation nanodiamonds, together with a clear realization of the wide area of their possible application, apart from the obvious direction as a material for polishing, has come at the beginning of this century. At this time, reports on detonation nanodiamonds have started appearing ever more frequently on the agenda of International “diamond” conferences. In 2003-2004, the first conferences dedicated to detonation nanodiamonds were held and the corresponding Bibliography indices have been published. The present-day interest in nanodiamonds is spurred naturally by current demands of nanotechnology.

In this paper we are going to address briefly specific aspects of the technology employed in DND production, discuss the present concepts concerning the structure of a single DND particle, and assess the main properties of nanodiamonds and their current and possible potential applications.

The paper is intended for University students and post-graduates with a broad range of interests who would wish to gain or extend their knowledge of novel carbon nanostructures.

In concluding this Introduction, it appears appropriate to give a definition to the subject of the present paper. By detonation nanodiamonds, DND, we are going to understand in what follows a species of synthetic diamond which is produced in detonation of an explosive from the carbon present in its composition. DND particles represent diamond crystallites with sizes confined in the 4-5 nm interval.

2. Technology of Production of Detonation Nanodiamonds

2.1. The Principle Underlying the Detonation Synthesis

We start with assessment of the principle underlying detonation synthesis, i.e., the technology employed in production of a material based on the use of explosion energy.

By explosion one conventionally understands fast transformation of an explosive to gaseous reaction products, a process accompanied by generation of a shock wave. Shock wave propagation in any medium entails intense dissipation of energy. Therefore,
stable propagation of a shock wave in a medium can be maintained only under a steady influx of energy. The source of energy for a shock wave in an explosion is the energy released in chemical transformation of the starting explosive into reaction products. The shock wave whose propagation through an explosive is sustained by the energy of chemical transformation is called the detonation wave.

The starting explosives can be composed of a combustible and an oxidizer, of attendant chemical compounds and their mixtures. The parameters of the detonation wave (its pressure and temperature) reached in the reaction of compound explosives can be varied by varying properly their starting composition.

The chemical reactions occurring in an explosion are similar to those sustaining combustion. Just as in the burning of organic materials in air, explosion entails formation of carbon dioxide from carbon, water from hydrogen, and elementary nitrogen from complex chemical compounds. Unlike conventional burning, however, which consumes oxygen of the air and proceeds, as a rule, in excess oxygen, the initial combustible to oxidizer ratio in the chemical reaction of an explosive transformation is set by the starting composition of the explosive. The energy spent to sustain the detonation wave in explosion is released only in the reaction of transformation of the starting explosive. This appears only natural, because all the other processes, which may be involved, namely, heat transport, diffusion and convection, to name just a few, occur at a much slower rate, i.e., they have long characteristic times. This is why detonation is treated usually as an adiabatic process. It is assumed that the linear dependence of detonation rate on the density of the explosive is a direct consequence of the adiabaticity of the process.

After the passage of the detonation wave, the chemical reactions initiated in the detonation products do not stop. The products of the detonation, for instance, water and the carbon oxides interact with one another in what is called secondary reactions. If detonation occurs in air, the detonation products undergo additional oxidation. A side effect is their dissipation in the atmosphere.

All this adds up to making experimental determination of the composition of the products of explosion a problem difficult to tackle. It is not less awkward to approach theoretically the equation of chemical reaction describing the explosion-induced transformation, with a possible exception of a few limiting cases. This places difficulties in the way of precise calculation of the heat released in the chemical reaction, which supplies the energy to the detonation wave. At the same time, predicting the parameters of a detonation wave from the composition and parameters of the starting explosive is a problem of considerable practical significance. To solve it, one is forced to invoke mathematical models of daunting complexity, which quite frequently cannot be approached except with the use of supercomputers.

There exists a simplified approach to the problem, which had appeared long before the advent of computers and is based on a theoretical model easy to grasp. By this approach, explosive transformation starts with formation of compounds, which provide the largest contribution to the energetics of the detonation process, namely, elementary nitrogen and water. The rest of the oxygen is assumed to undergo close to equilibrium
partition for the reaction \(2\text{CO} \Leftrightarrow \text{C} + \text{CO}_2\). The carbon to oxygen ratio in the detonation products is called usually the oxygen balance.

Considered within this simple model, all explosives can be divided into the following four main groups.

1. Explosives with a positive oxygen balance, with an amount of oxygen larger than that required for oxidation of the combustibles contained in the explosive. They are sometimes called oxidizers; belonging to this group is, for instance, the ammonium nitrate.
2. Explosives with zero oxygen balance, in which the amount of oxygen is exactly equal to that of carbon and hydrogen. The best known example of such an explosive is hexanitrobenzene. The combustible components are fully consumed in an explosion, with all of the carbon becoming converted to carbon dioxide.
3. Explosives with a weakly negative oxygen balance. The carbon to oxygen ratio is such that the amount of oxygen present is not large enough to ensure complete transition of carbon to \(\text{CO}_2\) but larger than required for the transformation to \(\text{CO}\), i.e., \(1 < \text{C}/\text{O} < 2\). The well-known examples of such explosives are trinitrobenzene and hexogen (RDX). See Figure 1.
4. Explosives with a strongly negative oxygen balance. For their carbon to oxygen ratio, the amount of oxygen is not large enough to provide complete transformation of carbon to \(\text{CO}\), i.e., \(\text{C}/\text{O} < 1\). This implies that part of the carbon will evolve in free form. The best known example of such an explosive is trinitrotoluene (trotyl). See Figure 1.

![Chemical formulas of trinitrotoluene (TNT) and hexogen.](image)

The elementary carbon released in detonation should naturally condense in the form, which is thermodynamically stable at the temperature and pressure (PT parameters) in the detonation wave.

Thus, if we devise a detonation process with a negative oxygen balance and with PT parameters corresponding to the region of thermodynamic stability of diamond (see Figure 2), it should in principle be possible to reproduce the explosive conditions conducive to diamond synthesis. It is this idea that underlies the detonation synthesis of diamonds.
The thermodynamic functions of diamond and graphite differ markedly. As a result, the heats of chemical transformation in an explosion will likewise be different, depending on the actual form in which the condensed carbon will evolve. Therefore, calculation of the detonation rate for explosives with a strongly negative oxygen balance yields two solutions, with one of them corresponding to precipitation of diamond, and the other, to that of graphite.

Figure 2. Phase diagram of carbon and the detonation parameters.

Secondary reactions, primarily oxidation of released carbon by atmospheric oxygen, preclude preservation of the carbon precipitating in explosion in the form of diamond, unless special precautionary measures are taken. Under certain conditions, however, the diamond formed in an explosion can be preserved. The diamond produced in this way is called detonation nanodiamond. Its earlier synonyms, particularly in the Russian literature, were ultradisperse diamond and explosive diamond. Quite lately, new terms have come into use - nanodiamond and ultrananocrystalline diamond. The latter term implies that the size of the diamond crystallite is less than 10 nm.

One more terminological remark may be appropriate here.

The terms “nanodiamond” and “ultrananocrystalline diamond” are used also when referring to polycrystalline diamond films obtained by chemical vapor deposition (CVD), in which the size of diamond crystallites is likewise confined to the nanometer scale. Therefore, diamonds produced in an explosion from the carbon of an explosive should be preferably defined by the attribute “detonation”.

Thus, in order to produce detonation diamond from carbon of an explosive, the following conditions should be met:

1. A strongly negative oxygen balance of the original explosive to ensure formation of condensed carbon in the reaction products;
2. The explosive to be used should have a power high enough to ensure thermodynamic stability of diamond in the PT conditions of the detonation wave. It is required to note that the first and the second conditions are partially contradictory;

3. The explosion should be performed in special conditions that would preserve the products of the explosion and suppress secondary reactions.

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Biographical Sketches

Alexander Vul’ was born in Krasnoyarsk, USSR in 1942. He graduated Moscow Institute of Steel and Alloys in 1965 as an engineer of semiconductor electronics. Then he was PhD student at Ioffe Physical Technical Institute, Leningrad, USSR where he obtained PhD in 1973.

He was appointed as researcher at Ioffe Institute in 1970, then as senior researcher (1974) and head of lab “Physics for Cluster Structures” (since 1993). Until 1993 his research had been related to physics of semiconductors and then physics of new forms of nanocarbon (fullerenes, nanotubes, nanodiamonds, etc). At the same time he was appointed as a senior lecturer and then as full professor (since 1994) at State Polytechnic University, St.Petersburg, Russia. He took position of Visiting Professor of Toyohashi Institute of Technology in Japan for one year starting from May 2000. He was one of the founders of the Biennial International Conference “Fullerenes &Atomic Cluster” in St. Petersburg, Russia (since 1993), and since 1997 he was appointed as a chair of the Program committee of the conference. His current research related to physics properties of carbon nanostructures, in particular detonation nanodiamonds and its applications.

Prof. Vul’ is author of more than 140 papers in refereed journals, 7 chapters of monographs, 28 inventions and patents; he made more than 90 presenttations at international conferences. He is member of Editorial Board of a Journal “Technical Physics Letters”, member of Editorial Advisory Board of an International and Interdisciplinary Journal “Fullerenes, Nanotubes and Carbon Nanostructures”, member of Scientific Council of Ioffe Physical-Technical Institute (since 1998), member of Scientific Council of the Russian State Program “Fullerenes and Atomic Clusters” (1994-2004), member of a Committee “Industry of Nanosystems and Materials” at the Russian State Agency of Science and Innovation (since 2004).

Alexander Aleksenskiy was born in Murmansk, USSR in 1956. He graduated Leningrad Technological Institute in 1980 as an engineer of chemistry technology. Then he was PhD student at Leningrad Technological Institute, Leningrad, USSR where he obtained PhD in 1984.

He worked at Leningrad Technological Institute since 1980 to 2005 year as a researcher in the field of organic chemistry. He was involved in development of methods of detonation nanodiamond purification. He was appointed as senior technologist at Ioffe Institute in 2006, then as senior researcher (2009). His current research related to chemical and physical properties of detonation nanodiamond and its
applications.

Dr. Aleksenskiy is author more than 15 papers in referred journals, 1 chapter of monographs, 2 patents. He made 5 presentations at international conferences.

Artur Dideykin was born in Leningrad, USSR in 1958. He graduated Leningrad Polytechnic Institute in 1981 as an engineer-investigator in astrophysics. At the same year he was employed to Ioffe Physical Technical Institute, Leningrad, USSR as research scientist. He was appointed as senior researcher at Ioffe Institute in 1993. In 1987 he has earned the PhD degree in physics of semiconductors and insulators. Until 1993 his research had been related to physics of semiconductors and then physics of nanocarbons. Since 1981 till now he works in Ioffe Institute St. Petersburg, Russia. Since 1996 up to 2006 he had a combine job in “Euclid”, company as IT engineer. He is an author of 20 papers in refereed journals. His research interests are structure and electronic properties of nanocarbons, field electron emission, electronic and atomic force microscopy, optical sensing.