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Nanodiamonds

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Properties

ABSTRACT

Purpose: Diamond nanoparticles have been found in DLC films, in detonation products of explosives and in some type of meteorites. In this paper the results of physico-chemical examinations - also in vitro and in vivo - of Nanocrystalline Diamond Powder Particles (DPP) and Detonation Nanodiamond (DND) are reported.
Design/methodology/approach: Material characterizations of DPP have been evaluated by using: Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), Auger electron spectroscopy (AES), microX-Ray Spectroscopy. Biological investigation based on: (a) in vivo and (b) in vitro examinations as well (c) clinical investigations – contact allergy.
Findings: It has been proven that Diamond Powder Particles (DPP) may act as antioxidant and/or anti-inflammatory factors when applied in living systems. It seems probable that reactions between the diamond surface and some biologically important molecules play a significant role in this process.
Research limitations/implications: The mechanism of antioxidant and/or anti-inflammatory behavior of DPP is not yet fully understood.
Practical implications: Nanocrystalline diamonds can be dispersed in a biologically acceptable carrier to form various compositions. DPP can be included in a cream having bioactive properties.
Originality/value: Bioactivity of Diamond Powder Particles.
Keywords: Nanomaterials; Diamond Powder Particles (DPP); Detonation Nanodiamond (DND); Bioactivity

1. Introduction

Special unique properties like biotolerance and mechanical strength must be received to applay materials for implants [1]. All of this requirements seems to be made by all allotropic forms of carbon. Without the element carbon, life as we know would not exist. Carbon provides the framework for all tissues of plants and animals. These tissues are built of elements grouped around in chains and rings made of carbon atoms.

Such an interesting element has obviously been investigated and because chemistry is based on outer-shell electrons (also known as the valence electrons), it is believed that the secret of carbon is hidden in these valence electrons. Out of six electrons surrounding the carbon atom nuclei, two are able to create chemical bonds. When certain amount of energy is spent, carbon atom is in the excited state and then four outer-shell electrons determine the variety of carbon structure as well in the chemical compounds as in the pure carbon modifications. In diamond lattice, each carbon atom is connected to four other ones. All valence electrons are involved in creating chemical bonds. Diamond crystal is an example of valence structure, because each atom of carbon, situated in tetrahedron, is connected with one another by a covalent bond.

Diamond in the form of microcrystals has been used extensively in industry for the past half century. Diamond nanoparticles have been found both in plasmachemical reaction products and in some meteorites about twenty years ago.

The presolar grains were firstly discovered and isolated by Lewis and coworkers in 1987 [2]. Many theories have been proposed to explain the formation of the extraterrestrial diamonds: chemical vapor deposition (CVD) from stellar outflows, impact shock metamorphism driven by supernovae, UV annealing of carbonaceous grains, radiation-induced mechanism. Mitura in 1987 has shown for the first time that nanodiamonds can be formed under low pressure, with assistance of electrons, in CVD process [3, 4]. Similar conditions occur in the space.

As a result of collisions between electrons and carbon atoms in a growing nucleus one of many electron configurations typical for carbon is formed; the final result is a formation of nanocrystals in the gas phase. The observations proved that the structure of these nanocrystals depends on the negative self-bias potential of RF electrode, that is on the electron temperature, i.e. kinetic energy of electrons in the plasma. There is a critical range of the electron temperature of plasma, i.e. the kinetic energy of electrons at which diamond microcrystals are formed. In another range microcrystals of carbines, graphite or powders composed of an amorphous polymer are formed [3, 4]. Also Roy's experiments confirmed that metastable formation of diamond from a hot gas at low pressures is possible [5].

The Centre of Excellence NANODIAM, which was establish in the Technical University of Lodz, will be conscious of historic necessity to fulfill the mission of integration, and will share our experience and ideas in participation in the integration process, especially in the field of nanocrystalline diamond and modification of carbon surface.

Dynamically expanding our knowledge in biotechnology requires constant, or even accelerated, development of new technologies in many areas, not least in the field of materials engineering. We want to meet these requirements by elaboration of new surfaces for biomedical needs. The experience in this matter strongly indicate that crystalline carbon is an ideal material for these purposes. But features of the prepared surface are dependent mainly on the conditions used for surface formation. The knowledge of the surface allows us to customize the carbon in the deposited carbon to get new and expected properties while retaining properties and attributes already known and accepted. Realization of the above requires the synergistic collaboration of several laboratories which have different profiles of interest and diverse but highly specialized equipment. We also must ensure the rapid and willing exchange of information. In this way, the Centre of Excellence NANODIAM will be an important, if not unique, contributor to the fast and reliable development of new technologies for biomedical applications.

Diamond as a material has got extreme properties: it is always the biggest and the best. It is the hardest known material, has the highest thermal conductivity, is chemically inert and wear resistant, its electrically insulating and optically transparent. These properties, either singly or in combination, make diamond of value in a wide range of extreme circumstances. For this reason, a lot of people during last few centuries have dreamt of making diamonds (as for centuries before that they dreamt of making gold).Unlike the case with gold, in the last few decades it has begun to be possible. In the end of the millennium we have artificial diamonds made by a range of methods. Of course many scientists dream to manufacture very big diamonds (and that begins to be possible, too, including in a process which mimics the natural methods of the Earth). Our aim is much more modest: it is to produce the smallest diamonds in the world! They are so small that it's possible to see them only by Atomic Force Microscope - a microscope so powerful that we can look at separate atoms. Imagine a very thin layer, so thin that it's a thousandth part of millimetre, and that this very thin layer consists of tiny crystals of diamond, so tiny that one diamond crystal is of the size of nanometers, one millionth of a millimeter.

2. Synthesis of diamond perticles

2.1. RF Plasma Synthesis of Diamond Powder Particles

The idea of Radio Frequency Plasma Activated Chemical Vapour Deposition (RF PACVD) method is to excite plasma in methane with nitrogen or other hydrocarbons with nitrogen in an RF electric field under reduced gas pressure of about hundreds of Pa.

The aim of the study was to determine the conditions and to explain the mechanism of a formation of crystalline inclusions, diamond powder particles (DPP), which are present in the amorphous warp of carbon films (see Figure 1).

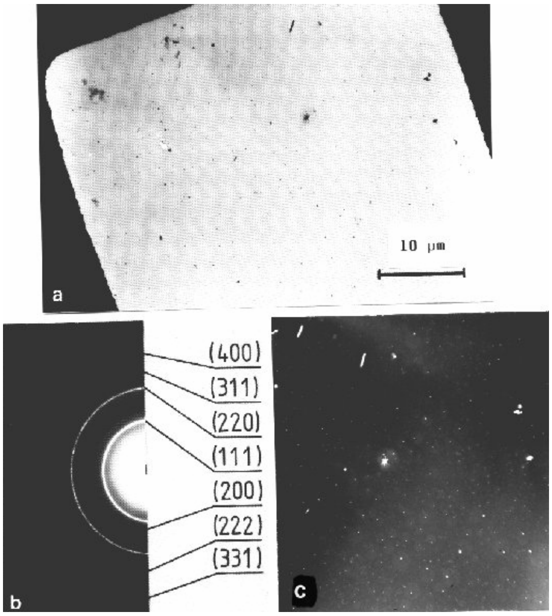

Fig. 1. Carbon film obtained by hydrocarbon decomposition in RF electric field (RF CVD), Philips TEM 300, a) image in the bright field, b) diffraction pattern (diamond), c) image in the dark field [3]

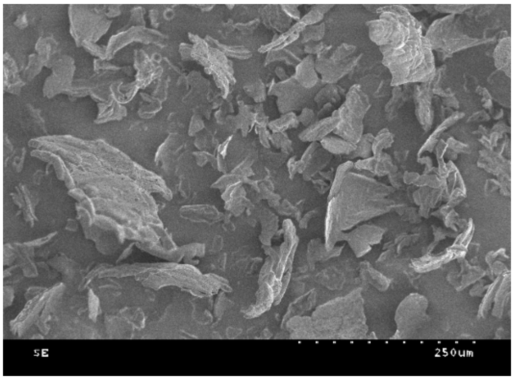

Fig. 2. SEM microscopic image of DPP synthetized by RF PACVD method

Typical carbon films formed by hydrocarbon decomposition in RF electric field are characterised by an amorphous structure with a few crystalline inclusions (compare Figure 1c). The author of the present paper assumed that the formation of crystalline inclusions can be a source of nanocrystalline diamond coating. NCD is a promising relatively cheap material for many industrial applications [6].

It is possibly to produce conglomerates of DPP with different shape (compare Figure 2).

The powders consist of aggregates of diamond nanocrocrystals, which can be shown on an electron diffraction pattern (Figure 3). Such crystallites built in into the layer are the nuclei of diamond crystallisation. The layers were deposited in a plasmachemical RF PACVD reactor is the most popular and very simple for thin films synthesis.

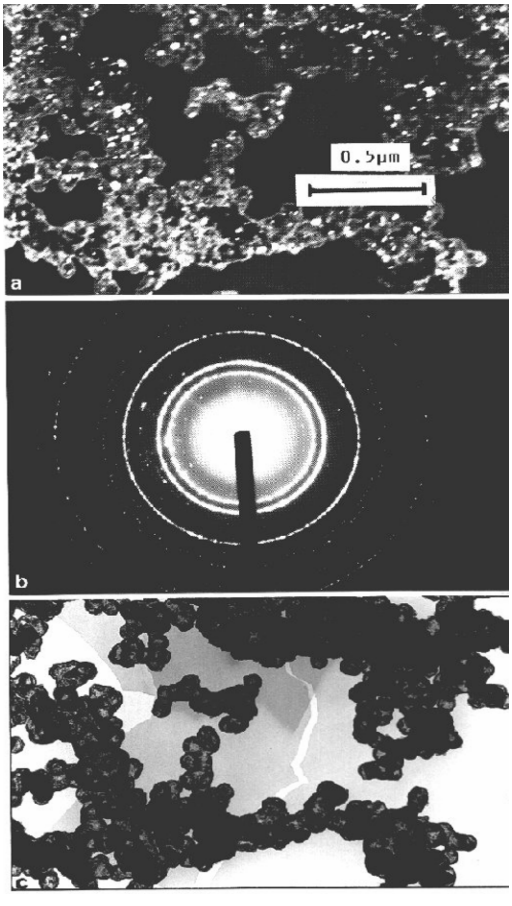

Fig. 3. Microscopic images of a fragment of an amorphous carbon film with diamond powder conglomerates, a) the image in the dark field, b) diffraction pattern (diamond), c) the image in the bright field [3]

The negative self-biased potential Ve, which is universal parameter in RF PACVD process characterising layer properties, is directly proportional to electron temperature, and taking into account plasma potential, it has effect on an average energy of ions which collide with the RF electrode. The parameter Ve determines the total energy transferred from plasma to the material during deposition.

By changing the negative self-biased potential of RF electrode and hydrocarbon pressure in the reactor, temperature of the substrate and ion energy can be affected. These are the parameters that have a direct effect on such properties of the layers: as hardness, energy gap, optical absorption and refractive index. It is connected to the structure of the material of the film.

2.2. The discovery of nanodiamond synthesis by detonation method

The history of the discovery of DND synthesis is unique. The discovery of diamond synthesis under static pressures at the end of the 1950s stimulated studies aimed at determining the application of explosion energy in diamond synthesis. For the first time, diamond was detected in a preserved shock-compressed graphite sample in the USA in 1961 [7].

About 40 years ago, in 1963, the detonation synthesis of nanodiamonds was discovered [8, 9].

V.V. Danilenko proposed and implemented (in 1962) ampoule-free synthesis with explosions in the explosion chamber instead of ampoule synthesis. Graphite was placed directly into a cylindrical charge consisting of a trotyl-hexogen mixture TG40; the charge was enveloped in a water jacket to suppress graphitization and reduce the unloading rate of the synthesized diamond.

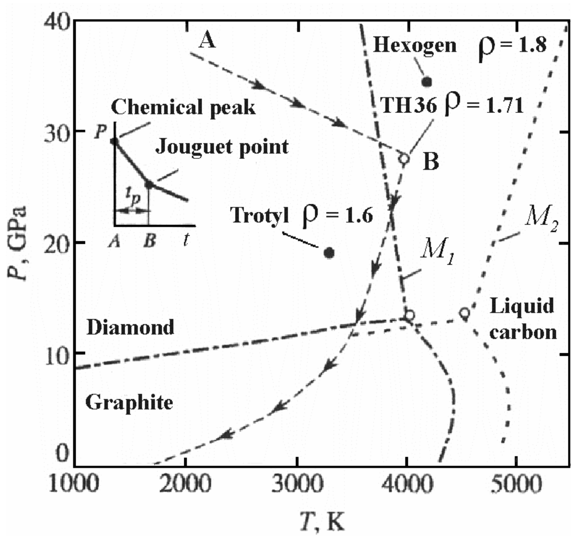

Fig. 4. Phase diagram of carbon and the detonation parameters. The inset shows the pressure profile in a detonation wave: *A* corresponds to the shock compression of the explosive (chemical peak), *AD* corresponds to the decomposition of explosive molecules with the formation of DPs and condensation of the free carbon (for an explosive with a negative oxygen balance) to DNDs at pressures higher than 20 GPa, *B* is the termination of the decomposition (the Jouguet point), and t_p is the duration of the decomposition. In the diagram, points *A* and *D* are indicated for the trotyl-hexogen mixture TH36, M_1 and M_2 are possible melting lines of carbon, and ρ is the density (in g/cm^3) [9]

Simultaneously, a comparison of the phase diagram for carbon and the parameters at the Jouguet point for the detonation of high-density charges of powerful explosives (the values of pressure and temperature obtained in DPs as a result of detonation-induced decomposition of explosive molecules) proved that the free carbon of DPs must condense in the form of diamond (Fig. 5).

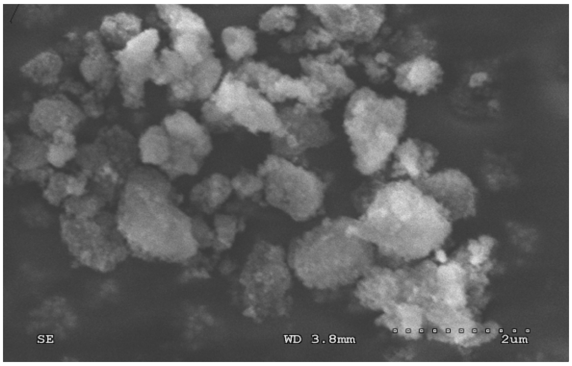

Fig. 5. SEM micrograph of conglomerates of DPP, manufactured by the detonation method

It can also be seen that, in order to obtain free carbon in DPs, an explosive with a negative oxygen balance should be used. Such explosive compounds simultaneously serve as sources of energy and carbon. As compared to diamond synthesis from graphite, the advantage of condensation of atomic carbon of DPs into diamond is that neither energy nor time expenditures are required for the destruction or rearrangement of the initial crystal lattice of graphite. Thus, the main problem lies not in the formation of DND but in its storage (i.e., in creating conditions that prevent oxidation and graphitization of the DNDs obtained).

3. Examination and results

3.1. Examination in vitro

All stress-responsive genes assayed by us were induced in the expected manner by the applied treatments.

Table 1.
Genes, encoded proteins and main inducing stimuli

Gene name	Encoded protein	Main inducing stimulus
JUN	Jun activation domain binding protein	Cellular stress
SODI	Cu/Zn superoxide dismutase	Oxidative stress
GADD45A	Growth arrest and DNA – damage	Genotoxic stress
FRAP1	FKBP– rapamycin associated protein 1	Genotoxic stress

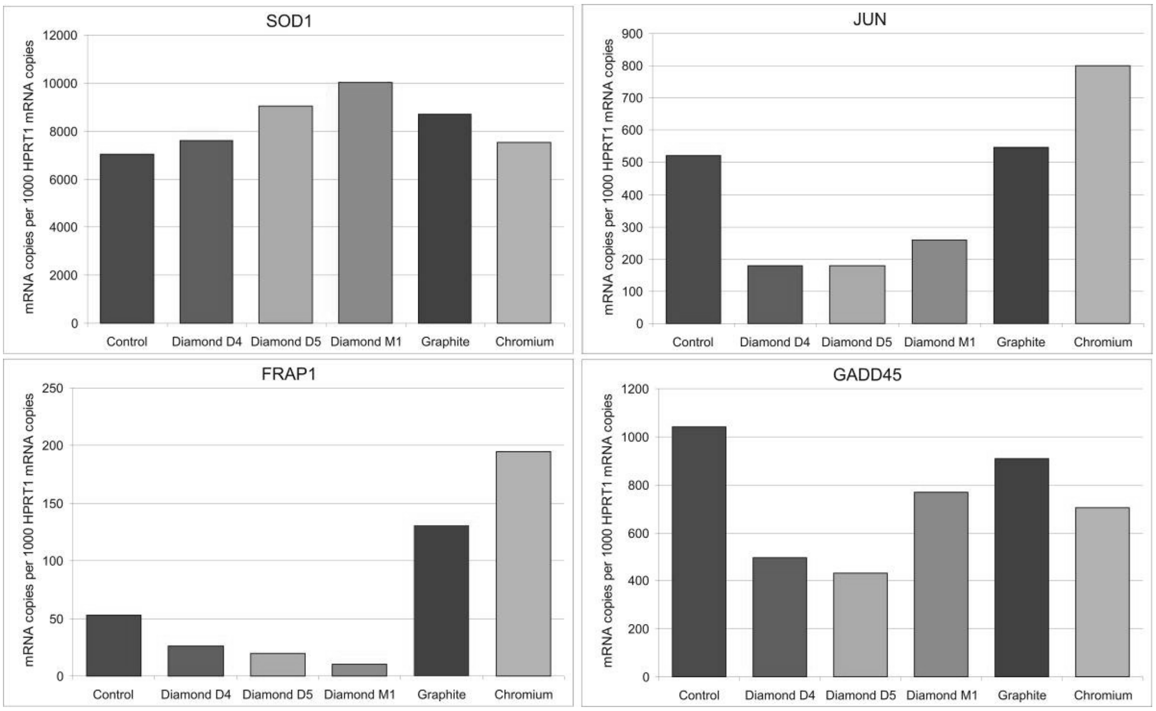

Fig. 6. Bioactivity of DPP's, as well as graphite and chromium powders, on gene expression (SOD1, FRAP1, JUN, GADD45). The control is the mRNA of the cells (human promyeloblastic leukaemia cell line HL60) without diamond, graphite and chromium powders. SOD1 gene decreases the oxidative stress (SOD is the antioxidant enzyme, its role is the inhibition of oxidative stress), FRAP1 and GADD45 genes influence on genotoxic stress, JUN gene influence on heat shock (cellular stress). The standard deviation is 5% [10]

The results indicate that the SOD1 gene decreases oxidative stress (SOD is the antioxidant enzyme – its role is the inhibition of oxidative stress), the FRAP1 and GADD45 genes influence genotoxic stress, the JUN gene influences heat shock (cellular stress). Results in Fig. 6 show the bioactivity of the DPP's as well as graphite and chromium powders on gene expression (SOD1, FRAP1, JUN, GADD45). The control is the mRNA of the cells (human promyeloblastic leukaemia cell line HL60) without diamond, graphite and chromium powders.

DPP influences the gene expression responsible for cellular stress (heat shock), genotoxic (cancerogenous) stress and oxidative stress. All DPP and graphite powder increase expression of the SOD1 gene which is responsible for the antioxidant reaction in human organism. The high level of mRNA copies in the presence of Diamond M1 demonstrated its antioxidant property. Chromium powder did not influence oxidative stress in the human body (i.e., it did not influence on SOD1expression).

All of the DPP's decreased the genotoxic stress which is responsible for cancer, the most significant decease was observed for Diamond M1. In contrast, graphite and chromium powders significantly increased the genotoxic stress (FRAP1). All the DPP's decreased cellular stress, graphite powder did not have any influence, and chromium powder increased cellular stress (JUN). All powders decreased the expression of GADD45 (genotoxic stress), but the most significant influence is for Diamond 4 and Diamond 5 powders [10].

3.2. Examination in vivo [11]

The investigation of biotolerance were made using stainless steel AISI 316L implants, passivated and coated with carbon layer, in laboratory animals. After the implantation of the samples the animals have quickly returned to the normal activity, there were no noticeable differences in their behaviour. X-ray investigations showed that the implants had been inserted correctly. No reaction or any changes around the implants were found in the x-rays. On the basis of the research it was found that in subcutaneous tissue, muscles and bones, thin connective tissue capsules built from fibrocytes and collagen fibres were formed. In the wall of the capsule neither a phagocytic reaction was observed nor products of corrosion were found [11].

Internal organs (liver, kidneys, spleen) did not show any pathomorphological changes.

The histopathological investigations showed a very good biotolerance of the implants coated with the NCD layers. The coating protects efficiently against corrosion and metalotoxemie.

3.3. Clinical research - Antiallergic barrier diffusion

The patch tests on the human back skin are based on the examination of contact allergy on nickel (Ni) in presence of Diamond powder 1 and Diamond powder 2 and Elocom. The method of patch test is described in [12].

Samples coated with carbon coatings and implanted under human skin characterize biocompatible with contact allergy on molecular level. This phenomenon is explained following: Nanocrystalline Diamond Coatings is diffusion barrier which determine blockade diffuse of metal ions into tissue [12].

Diamond powders inhibit contact allergy on nickel in comparision with treatment by Elocom (Figure 8).

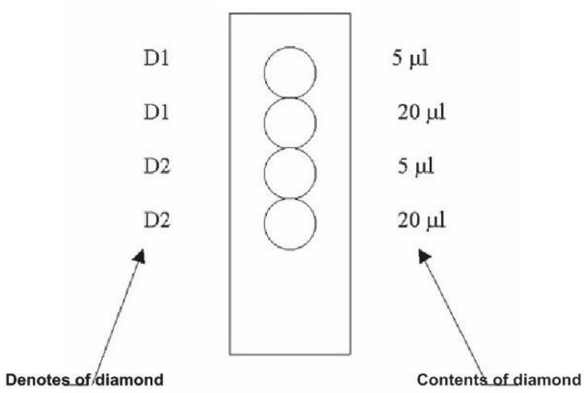

Fig. 7. Procedure of preparation of patch test with diamond in human back skin

Fig. 8 The patch tests with DPP1 and DPP2 [13,14]

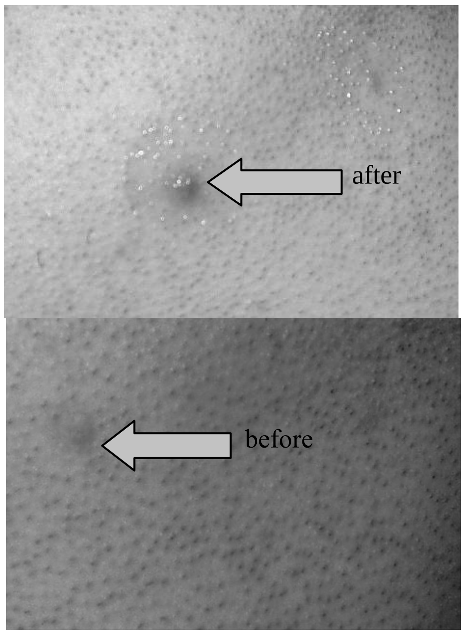

Fig. 9. Paramedical substance in treatment of bacterial skin diseases (staphylococcus aureus, staphylococcus epidermidis, streptococcus pneumoniae)

3.4. Clinical research - Antiallergic cream

Nanocrystalline diamonds can be dispersed in a biologically acceptable carrier to form various compositions. DPP can be included in a cream having bioactive properties.

Bakowicz [11] used such a paramedical substance in treatment of bacterial skin diseases (staphylococcus aureus, staphylococcus epidermidis, streptococcus pneumoniae).

4. Discussion

Carbon coatings of metallic implants - as the materials to be inserted into human body, have satisfy the following requirements: biocompatibility (haemocompatibility and histocompatibility), chemical stability, biostability and excellent adhesion and very good mechanical characteristics. However, not only biocompatibility is very important but bioactivity also and it's still investigated on molecular level. The patch tests with indicate that diamond powder is biocompatible biomaterial for human skin in patients with contact allergy. Moreover, Diamond Powder Particles inhibits lipid peroxidation in blood plasma and inhibits haemolysis in vitro examinations. Haemolysis is the process in human body which is connected with damage of red blood cells. The result of haemolysis is the cutting short of its life time. The reasons of the first type of haemolysis are the defects in erythrocyte membrane skeleton. This type of damage of erythrocytes is the haemolysis caused by factors in the same red blood cell: membrane structure and its enzymatic system and the structure of hemoglobin.

Diamond Powder is a potential medicine because in examinations in vitro and in clinical research has antioxidant, antiinflammatory, anticancerogenic and antiallergic properties.

5. Conclusions

It has been proven that Diamond Powder Particles (DPP) may act as antioxidant and/or anti-inflammatory factors when applied in living systems. The mechanism of such behavior is not yet fully understood. It seems probable that reactions between the diamond surface and some biologically important molecules play a significant role in this process.

Nanocrystalline diamonds can be dispersed in a biologically acceptable carrier to form various compositions. DPP can be included in a cream having bioactive properties.
Diamond Powder is a potential medicine.

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