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Nanocrystalline diamond, its synthesis, properties and applications

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Materials

ABSTRACT

Purpose: Carbon constitutes a principal component of a living organism. A man, weighting 100 kg, carries in his body approximately 12 kg of pure carbon. In the nature, carbon occurs in several allotropic forms, such as diamond, graphite (including nanotubes and fullerenes) and carbines. A new type of carbon material, nanocrystalline diamond formed by the decomposition of methane in a process of radio frequency plasma activated chemical vapor deposition (RF PA CVD) is presented.

Design/methodology/approach: Nanocrystalline diamond (NCD) films were synthesized with a new method, employing dense radio frequency plasma. The idea consists in a decomposition of methane in radio frequency (13.56 MHz) plasma.

Findings: One of the most important property of NCD is the protection living organism between the metalosis. NCD forms the barrier diffusion between implant and human environment.

Practical implications: Advanced medical studies, concerning a use of medical implants coated with nanocrystalline diamond enabled their practical applications.

Originality/value: The most interesting property of diamond is the fact that it can play the role of electrodonor. This is directly associated with the new type of bioactivity, exhibiting by diamond.

Keywords: Nanocrystalline diamond; Biomaterials; Implants; Carbon coatings

1. Introduction

Carbon, as a material compatible with a living organism, has found an application in medicine [1-5]. Coating of medical implants, i.e. implants for cardiosurgery, orthopaedic surgery, dentistry etc., with nanocrystalline diamond (NCD) films appears particularly interesting [5].

Carbon biomaterials are characterized by the following properties:

- good biological tolerance in an evironment of systemic tissues;
- resistance to radiation, both ionizing and non-ionizing;
- blood compatibility;
- athrombogenity;
- specific physicochemical properties.

An application of nanocrystalline diamond films in medicine opens new intellectual horizons for a contemporary human, and allows for an enrichment of the present knowledge, technology and thought with elements, which are not completely understood but which in a significant way contribute to the development of technical applications in medical science. Diamond layers are getting a more and more significance in medicine, becoming a biomaterial of the highest, unmatched by other materials, degree of biocompatibility with the environment of human body.

Up to now, an application of any biomaterials induced controversies and stirred not always fruitful discussions of scientific circles. Naturally, this was in the first place connected with the problem of an effect of an implant, as a “foreign body”, on the human organism. Being afraid of a proliferation of toxic effects of an implant on the surrounding cells, tissues and organs, such an attitude blocked developments of further and more specialized applications of implants in medicine.

Multidirectional studies pointed out to a high toxicity of medical implants, automatically disqualifying certain materials due to their carcinogeneity (titanium, nickel and chromium implants), cytotoxicity (implants made of nickel, chromium and austenitic steel), a presence of allergic reactions (nickel, molybdenum and chromium implants), a presence of immunological reactions (implants made of nickel, austenitic steel and chromium-molybdenum steel), a presence of inflammatory reactions in the tissues and organs surrounding an implant (due to mechanical irritation and following damage, leading to a cascade of an inflammatory reaction, including an influx and activation of inflammatory cells and a release of inflammation mediators and resulting in a macroscopically evident hyperaemia, inflammatory infiltration and a proliferation of fibrous tissue – mainly observed in a connection with metal implants).

The presence of an implant in a living organism is undoubtedly accompanied with its reactivity, i.e. with a certain degree of its interaction with an organism, affecting this organism's homeostasis. When an implant placed in the internal environment of a system significantly interferes with this system's proper functioning, then such an unwanted bioreactivity of the implant, in spite of sometimes its very good mechanical parameters, does not fulfill a definition of biocompatibility as a principal criterion of a functioning of a biomaterial in the organism.

The notion of biocompatibility is connected with a bipolar definition, comprising a mutual effect of both elements: implant-organism and organism-implant. Only such a symbiosis allows a given material to fulfill biocompatibility criteria and to find an application.

This is because one should not forget the effect of an organism on the implant. The aggressiveness of the internal environment of a system on medical implants is very high. A damage done to an implant is very disadvantageous for the system, because it disturbs its functioning, often leads to its serious impairment, at the same time renouncing the implant's principal utility function.

The question whether a given biomaterial is safe can only be answered by e set of specialized medical investigations, authorizing the application of an implant in medicine, and comprising a number levels, on which a rational interaction between an implant and an organism takes place.

The studies on diamond layers, covering medical implants, point to their certain unique properties, giving rise to a new modernized attitude towards such notions as biocompatibility, biotolerance and bioactivity of an implant, or rather those of a coating applied to it, which constitutes a contact point of two surfaces of completely different and sometimes even antagonistic properties. As it is easy to guess, due to a large variety of implants with respect to both their material and application aspects, a proper selection of a biocompatible coating, able to isolate an implant from the environment of a human organism and to prevent all the, generally speaking, unwanted reactions taking place in the organism, is a very important and undoubtful task.

Results of the newest studies on nanocrystalline diamond coatings applied to medical implants, show that diamond as a biomaterial exhibits high biocompatibility and positive bioactivity, what puts it on unrivaled leading position among the up-to-date used biomaterials and broadens the notion of biocompatibility.

A series of studies on diamond films, performed on different levels, was carried out. These levels were:

- the first level consists in a division between the studies conducted *in vitro* and those performed *in vivo*;
- the other levels comprise studies exploiting those *in vitro* and *in vivo* techniques, which serve the purpose of an assessment of a safety and usefulness of a deposition of medical implants with nanocrystalline diamond coatings

The following are the levels of these highly specialized and differentiated studies:

<u>macroscopic level:</u> inflammatory reactions, allergic reactions, cytotoxic reactions, corrosion resistance test – a Tyrode fluid simulation, corrosion resistance test – a 2% HCl solution simulation, environmental exposure to systemic fluids test, biological corrosion tests, biocompatibility testing (comprising haemo-compatibility, histo-compatibility and cyto-compatibility tests), toxicity tests (metallosis)

<u>molecular level:</u> enzymatic tests (testing the activity of catalase, suboxide dismutase, glutathione peroxidase, lipoxygenase in the presence of octadecatrienoic acid as a substrate, lactate dehydrogenase), thrombogenicity tests (a continuation of haemo-compatibility investigations), immunocytochemical testing, sanitary and chemical testing, cell cultures, testing cytotoxic reactions (spectrophotometric methods of measurement of a concentration of the products of lipid peroxidation – biological membrane damage), potential degree of mutageneity and carcinogeneity (lipid peroxidation – DNA damage) tests, testing inflammatory reactions – testing the viability of neutrophilic granulocytes under conditions of a presence of LPS and FMPL bacterial endotoxin as a standard, biocompatibility tests

<u>clinical level.</u>

2. Carbon and its allotropic forms [5-11]

2.1. Diamond

In its crystalline unit cell (Figure 1), diamond contains 8 atoms. The coordination polyhedron is a tetrahedron. The coordination of a carbon atom reflects a spatial distribution of its σsp^3 hybridized electronic orbitals. Atomic bonds are directed from a central atom towards the vertexes of the tetrahedron, forming with each other angles equal 109.5^o. The shortest distance between atoms amounts to one fourth of a diagonal of the spatial unit cell. A distance between diamond atoms in the crystallographic direction [100] is equal 0.154 nm. Diamond structure can be regarded as a face centered cubic (FCC) lattice of the A_1 type, in which fifty percent of tetrahedral interstices are occupied by carbon atoms.

When the [111] direction of diamond crystalline structure is positioned vertically (Figure 2), folded hexagonal rings with centers of carbon atoms placed in their vertexes are seen in the (111) plane, situated horizontally.

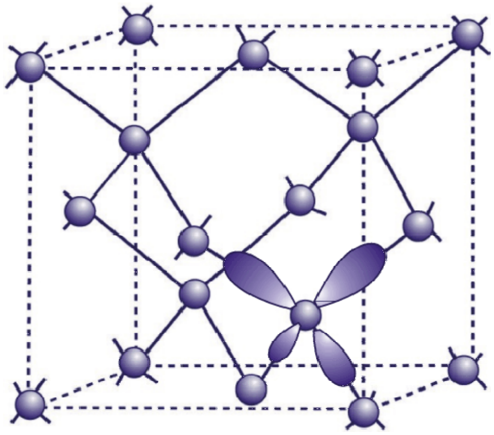

Fig. 1. Diamond crystalline unit cell with the electronic structure (four σsp^3 orbitals) of one of the atoms marked

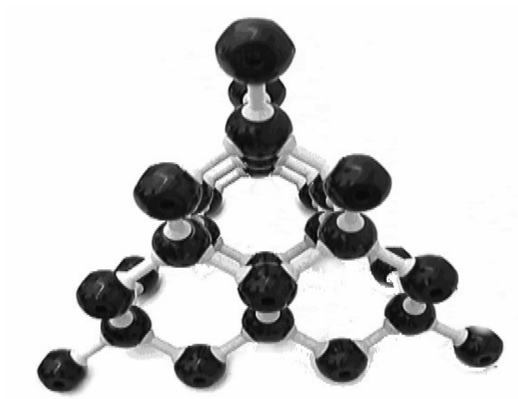

Fig. 2. A model of diamond crystalline lattice with a view of the (111) plane

The (111) planes are diamond planes of cleavage. The space filling factor in the diamond structure is low and it amounts to 34%.

The largest natural diamond ever found by man was called Cullian. Its weight amounted to 3106 carats and it consisted of approximately 10^{30} carbon atoms. After having been cut and ground, it was made to 105 brilliant pieces, including most famous jewels of the British Crown, Cullian I and Cullian II, stored in the Royal Treasury Tower in London.

Hexagonal diamond – londsdeilite

Lonsdeilite is sometimes called hexagonal diamond, since its structure and properties are similar to those of diamond. This is due to the fact that lonsdeilite also posseses the σsp^3 type of bonds. The (001) planes of lonsdeilite are identical with (111) planes of diamond. The lattice constants are: a_o = 0.252 nm and c = 0.412 nm. The distance between the closest carbon atoms is the same as it is in diamond and it amounts to 0.154 nm.

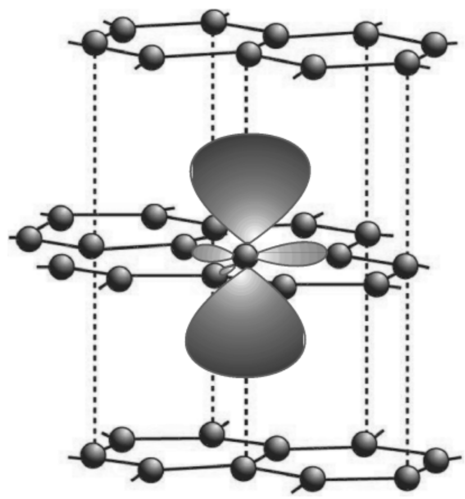

Fig. 3. Graphite crystalline unit cell with the electronic structure (three planar σsp^2 orbitals in (001) plane and one $p\pi$ orbital) of one of the atoms marked

2.2. Graphite

Graphite is an allotropic form of carbon, stable under normal pressure and temperature conditions. A crystallographic lattice of graphite, with the unit cell marked, is presented in Figure 3.

Graphite has a typical laminar structure. Atoms are placed in layers, forming hexagons in the (001) plane, with the interlayer distance being 0.142 nm. In the layer, each carbon atom has three closest neighbours. The coordination figure is an equilateral triangle. The space filling factor is equal 16.9%, with an assumption that only covalent bonds are present in the structure.

Strong covalent bond, formed of hybridized electronic orbitals σsp^2, connect carbon atoms in (001) planes. The fourth electron of each atom is in a state of resonance between three adjacent atoms, forming a weak transitional $p\pi$ bond with the atoms of neighbouring layers. The bonds within the (001) plane are much stronger than the bonds between (001) planes and, as indicated by interatomic distances, they are also stronger than diamond bonds.

As a result of substantial differences in carbon-carbon bond strength between atoms in one layer and atoms of adjacent layers, graphite is characterized by a strong anisotropy of its physical properties (cleavage, thermal expansion, electrical conductivity, thermal conductivity).

Fullerenes and nanotubes

First suppositions concerning a reality of polyandric carbon molecules appeared in astrophysics. In the seventies of the last century, Russian chemists theoreticians confirmed their potential existence. Since then, not only their existence been has demonstrated, but molecules, comprised of several dozen carbon atoms, have already been synthesized.

In May 1990, Wolfgang Krätschmer of the Institute of Nuclear Physics in Heidelberg and his student Konstantinos Fostiropoulos were working on a special method of obtaining benzene. Soon, a synthesis of C_{60} – a molecule of carbon in a form of a football, comprised of twenty regular hexagons and twelve pentagons (Figure 4), was reported. As it quickly turned out, this was not the only stable "hollow" polycarbon molecule.

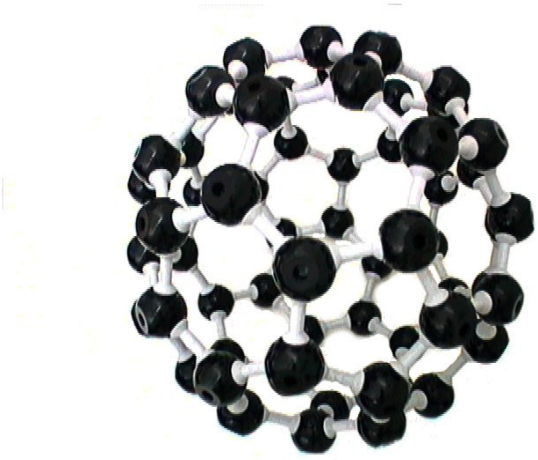

Fig. 4. A model of fullerene C_{60} molecule

Robert Curl and Richard Smalley identified a stable molecule, consisting of 70 carbon atoms (C_{70}) – 25 cubes – and compared it to a rugby ball. To pay tribute to an American architect of the fifties, whose designs were based on regular polygons, the new class of carbon molecules was given a term of fullerenes. Today we know that there exist molecules of the formulas C_{84}, C_{180}, and probably also C_{240} – all in a form of a "closed container", thus making a C_n class of compounds. Molecules of carbon compounds, for instance molecules of the $C_{60}M^{P+}$ type, where p is an integer and M is metal atom, such as lanthanum or potassium, locked in a C_{60} sphere, are synthesized. Also intelligent medications, aimed at directly reaching sick cells, can be placed in the fullerene sphere.

Fullerenes constitute an entirely new class of materials, exhibiting properties, which are relatively easy to determine and to design. It is their exceptional stability as well as advantageous electrical and magnetic properties, that draw significant scientific attention to these compounds, in particular in the context of high capacity battery design and semiconductor technology in general. First reports concerning medical applications of fullerenes have also appeared.

Carbon nanotubes (Figure 5) were synthesized in the laboratories a few years ago. Their extraordinary properties, mechanical and electrical properties in particular, focused enormous interest. Carbon-carbon bonds, present in the plane of a nanotube, belong to the strongest chemical bonds found in the nature. This is a reason why their tensile strength in unmatched by any other material. There exists a project aimed at a construction of a cosmic rope for the purpose of hoisting space vehicles to their orbit. Preliminary studies in this area are extremely interesting.

An opportunity also appears to incorporate either single atoms or entire complexes, in order to modify features of the material produced. It seems that nanotube based fibers may constitute one of materials of the XXI century.

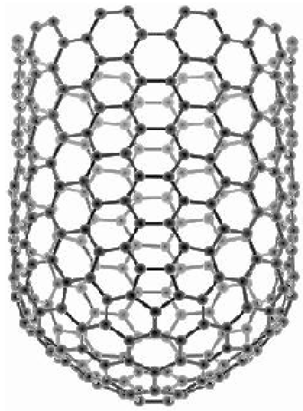

Fig. 5. Structure of nanotube

2.3. Carbine

Carbine constitutes the allotropic form of carbon that has been relatively least studied. The first report concerning carbine was, published in the sixties, work of Gorsey and Donney dealing with the discovery of the so called chacite or Ries crater carbon (taking its name from that of a meteorite produced crater, in which this form of carbon was found). According to the authors hypothesis, chacite was created from graphite, shortly before the meteorite impact, when it was subjected to high temperature and pressure. At the same time, Kasatotschkin and his coworkers carried out theoretical and experimental studies concerning a carbon polymer, which they called carbine. They made an asssumption that both diamond and graphite are of a polymer nature; diamond is a saturated polymer and belongs to the group of paraffins while graphite, being also saturated, was classified as an aromatic polymer.

Today, a few forms of carbine are known, among which the most important and the best understood are:

- **α-carbine**, which contains acethylene bonding (-C=C-), and this is why it can be described as polyacethylene; hexagonal unit cell, z=144, a_o=0.892 nm, c_o=1.536 nm, density $\rho=2.68\times10^3$ kg m^{-3}
- **β-carbine**, which contains cumulene bonding (=C=C=), and this is why it can be described as polycumulene; hexagonal unit cell, z=72, a_o=0.824 nm, c_o=0.768 nm, density $\rho=3.13\times10^3$ kg m^{-3}.

3. Synthesis of nanocrystalline diamond films [12-17]

A new type of material, nanocrystalline diamond formed by the decomposition of methane in a process of radio frequency plasma activated chemical vapor deposition (RF PA CVD) is presented below.

The films synthesized were investigated with respect to their structure as well as to their biological and chemical resistance and mechanical stability. In addition, studies were carried out with the help of energy dispersive X-ray analysis (EDX), Raman spectroscopy, atomic force microscopy (AFM), Auger electron spectroscopy (AES), corrosion tests, electrical break-down potential tests and preliminary clinical tests.

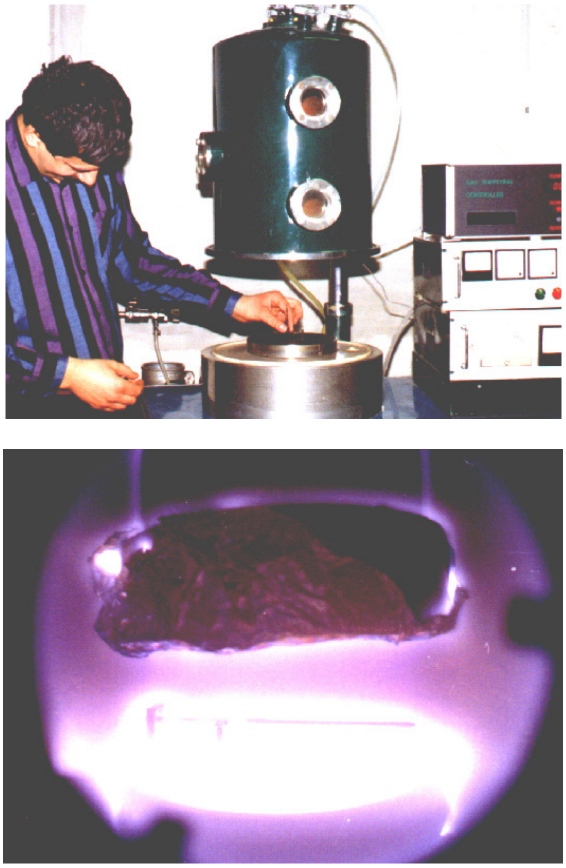

Fig. 6. The chamber of a plasma reactor with an orthopedic bold placed on a radio frequency driven electrode (left) and a discharge initiated in a radio frequency electrical field (right)

Nanocrystalline diamond (NCD) films were synthesized with a new method, employing dense radio frequency plasma. The idea consists in a decomposition of methane in radio frequency (13.56 MHz) plasma at a pressure of 20-400 Pa. A view of a reactor chamber with an orthopedic bold placed on a radio frequency driven electrode and a discharge initiated in a radio frequency electrical field are presented in Figure 6.

4. Bioactivity of diamond powder

Nanocrystalline diamond films exhibit high biocompatibility (compare Figure 7) with a human organism, but a complex interaction with an organism cannot be judged solely on the basis of these studies.

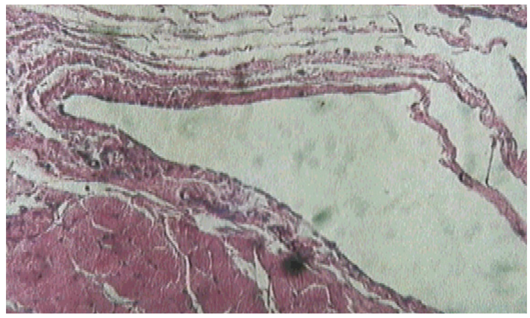

Fig. 7. A muscle. A capsule of thin connective tissue with small vessels. An implant coated with a thin film of nanocrystalline diamond 26 weeks after an implantation. Staining H.-E., magnification 100X

Studies concerning the effect of diamond powder [17, 18, 19] on a molecular level give an opportunity to assess this interaction, at the same time contradicting an opinion of this material's biological impartiality. Results, perceiving to a bioactivity of a nanocrytalline diamond powder, have been presented. This has a direct association with the properties of a nanocrystalline diamond film, which is nothing else but a collection of its crystallites.

An inhibition of toxic biochemical processes, connected with lipid peroxidation, by diamond powder constitutes an information, which brings completely new notions concerning biological properties of diamond and its potential applications as a biomaterial.

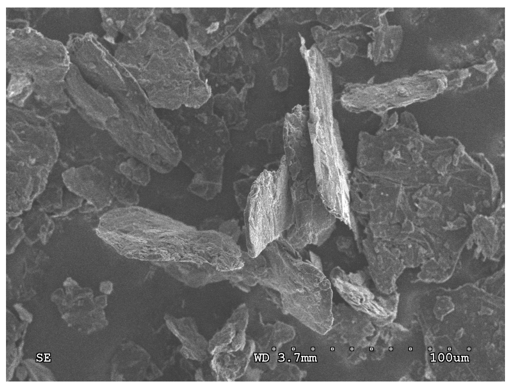

Fig. 8. A SEM microscopic image of carbon powder, synthetized with the RF PA CVD method

The process of lipid peroxidation is of a free-radical character and it contributes, to a large extent, to the pathogenesis of such diseases as diabetes mellitus, ischaemic heart disease, Alzheimer disease, chronic granuloma. This is a reason why the proven beneficial properties of diamond classify this material very high in a family of biomaterials, practically allowing for its unlimited applications in medicine (medical implants).

The application targets of diamond as a biomaterial are undeniable. However, its diagnostic and therapeutic perspectives require numerous studies and verifications, which ultimately should qualify nanocrystalline diamond powder to the compounds exhibiting therapeutic activity.

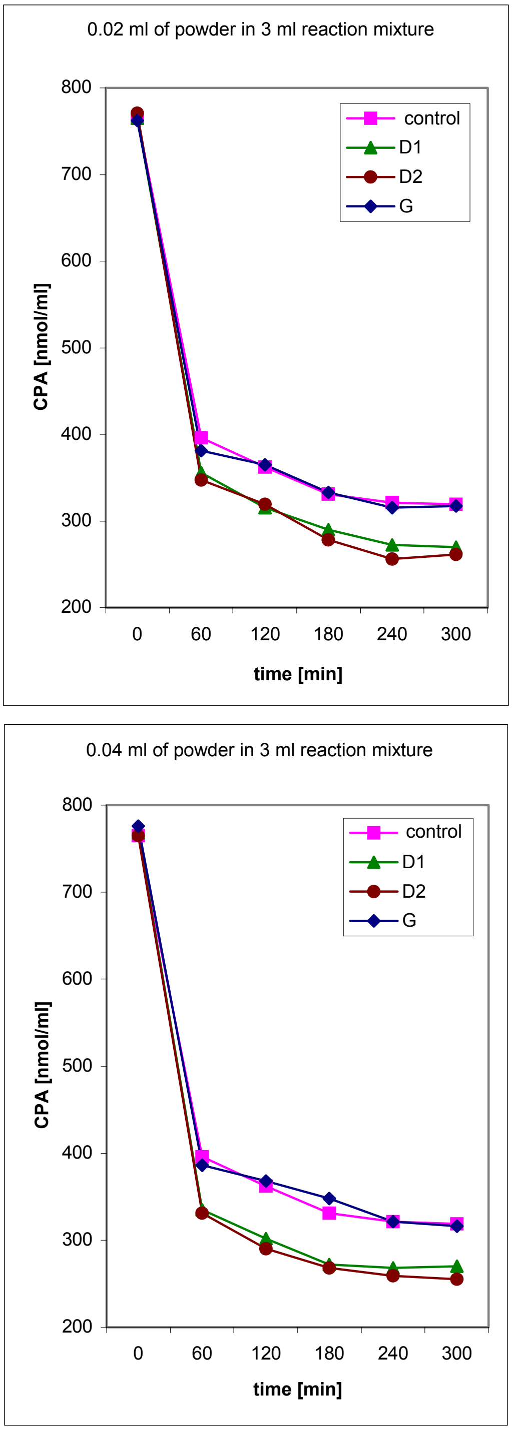

Fig. 9. Antioxidative ability of blood plasma in a presence of carbon powders

The most interesting property of diamond, discovered not a long time ago, is the fact that, in contact with water, it can play the role of electrodonor [20]. This is directly associated with the new type of bioactivity, exhibiting by diamond. Diamond powder takes place in chemical reactions as a heterogenic catalyst. The new type of biological activity of diamond, entirely different from that of ceramic biomaterials with controlled tissue reactivity and of resorbable ceramic biomaterials, consists in the fact that the reaction occurs in the presence of diamond, playing a role of a catalyst and not a substrate [20].

Diamond powder is not consumed in the chemical reaction, but its presence accelerates it. This is associated with antioxidant properties of diamond powder. Just as it is a case in any red-ox reactions, all the antioxidants known up-to-day change their oxidation state when they participate in the antioxidation reaction. Diamond powder is the only antioxidant, whose activity is not connected with a change of its oxidation state. When acting as a catalyst, it scavenges free radicals and inhibits peroxidation of polyunsaturated fat acids and a formation of lipid peroxides. Diamond powder is the only antioxidant of a catalytic mechanism of an inhibition of lipid peroxidation reactions. As a biomaterial, coating medical implants, it exhibits an entirely new type of biological activity [20-22].

The results of studies on diamond powder have explicitly shown that this material is biologically active and that it has a very positive effect on a number of toxic biochemical processes on a molecular *in vitro* level.

This material is also active on a cellural level, inhibiting an inflammatory reaction *in vitro*.

In clinical studies, in a contact with a skin of allergic patients, it does not induce allergic reactions (Figure 10).

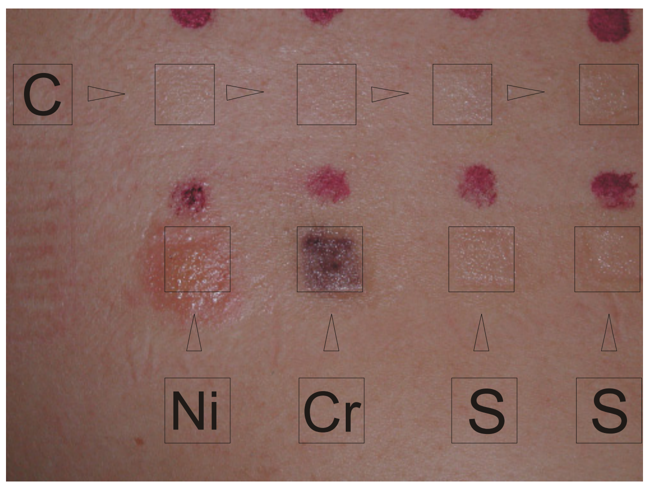

Fig. 10. By the lower markers, an allergic reaction of patient 6 to nickel and chromium(Ni – nickel, Cr – chromium, S – standard) can be observed. By the upper markers no allergic reaction to the powder of nanocrystalline diamond (C – carbon) is observed with the same patient.

5. Applications of nanocrystalline diamond [23, 24]

Advanced medical studies, concerning a use of medical implants coated with nanocrystalline diamond enabled their practical applications. For the first time, such devices were implanted in Pabianice (Dr Paweł Witkowski, under the supervision of Professor Kristian Zołyński) to a patient with a complex fracture of femoral bone, after standard metal implants (made of medical steel) had been rejected twice. After the surgery (see Figure 11), no symptoms of another rejection were observed, what enabled a continuation of the therapeutic process without any disturbances.

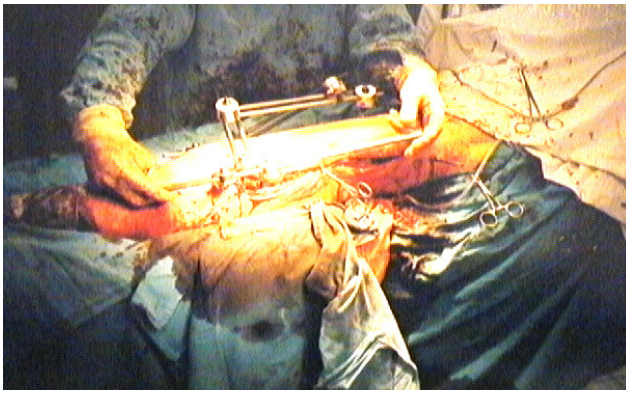

Fig. 11. An implantation of orthopaedic screws, coated with NCD film, into a human organism (Pseudoarthrosis femiris sin. Ostitis post fracturam apertam olim factam)

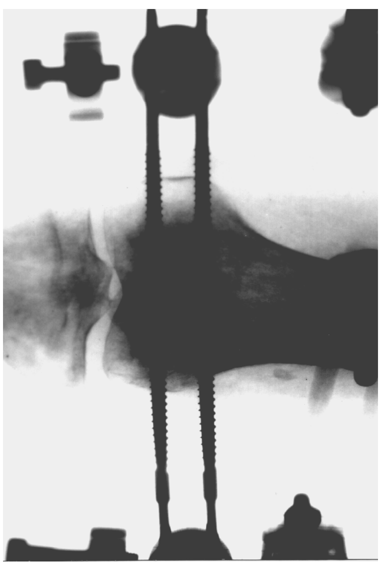

Fig. 12. An X-ray radiogram taken after an implantation of orthopaedic screws, coated with NCD film, into a human organism

After positive results of preliminary surface studies of an endoprothesis of femoral joint, carried out in Lyon (with Professor Patrice Couvrat) and in Bratislava (with Professor Marcel Zitnansky), also this element has been implanted into a living organism (Figure 13).

Fig. 13. Endoprothesis of a hip joint, coated with NCD film

6. Colour carbon films for the jewelry industry [25]

Low temperature plasma synthesis of nanocrystalline diamond allows one to produce coloured carbon films. This technology has been supported by a computer simulation of the synthesis process, developed in the framework of a PhD thesis of Dr Marian Cłapa. These achievements were presented in the years 1999-2000 in the Science Museum in London at the exhibition "Carbon coatings onto stainless steel", mainly presenting medical implants coated with a coloured nanocrystalline diamond (NCD) films. They drew an attention of Ms. Wendy Ramshaw, a British jewelry designer, who proposed a co-operation. One hundred of Millenium Medals, handed during official state visits by Elisabeth the Second, Queen of the United Kingdom, were manufactured.

The jewelry products of Ms. Ramshaw, equipped with coloured diamond coatings, were exhibited in 2000 at the *Millenium Exhibition* in the Contemporary Art Museum in London.

Fig. 14. A tiara, made for Queen Elisabeth the Second in the frames of the Calouste Gulbenkian Foundation project. Material – AISI 316L medical steel with a coating of nanocrystalline diamond

A crowning of the method's implementation was a production, in the frames of the Calouste Gulbenkian Foundation project, of a tiara made of medical steel coated with nanocrystalline diamond (see Figure 14). The tiara was produced for the celebration of the fiftieth anniversary of the crowning of the Queen Elisabeth the Second and, what is worth mentioning here, the Mother Queen had at that time an implanted endoprothesis of a hip joint.

We are accustomed to the fact that the price of diamond is very high. It is particularly high in the case of a jewelry diamond, ground to a brilliant. However, technological advances of the end of the XX century allowed for such cost lowerings of the processes, that diamond coatings applied in medicine increase the prices of implants to a minimal extent (!!!) only.

7. Conclusions

- Nanocrystalline Diamond Coatings (NCD) now is the best material which can be used in medicine onto medical implants and surgery tools.
- One of the most important property of NCD is the protection living organism between the metalosis, therefore different medical implants are covering with success by Nanocrystalline Diamond Coatings (NCD). NCD forms the barrier diffusion between implant and human environment and this phenomenon proved that diamond layers are biocompatible with living organism.
- Diamond Powder Particles (DPP) is an extended surface of NCD. DPP has positive influence on cells, tissues and organs in human organism. This is associated with antioxidant properties of diamond powder. Diamond powder is the only antioxidant, whose activity is not connected with a change of its oxidation state.

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