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Carbon coatings for medical implants

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Materials

ABSTRACT

Purpose: In this paper we report in vitro and in vivo results of Nanocrystalline Diamond Coatings which are used in medicine onto medical implants The very important property of carbon coatings is the protection living organism against the metalosis. Different medical implants with complicated shapes are covering by Nanocrystalline Diamond Coatings by RF dense plasma CVD.
Design/methodology/approach: 1) Material characterizations of deposited coatings have been evaluated by using: Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), Auger electron spectroscopy (AES), microX-Ray Spectroscopy and bend test 2) Biological investigation based on: (a) in vivo and (b) in vitro examinations as well (c) clinical investigations – contact allergy.
Findings: It was revealed that Nanocrystalline Diamond Coatings form the barrier diffusion between implant and human environment as a consequence prevent leaching of metallic ions into the body. Additionally, the research on carbon coatings proved that diamond layers are biocompatible with living organism. Contact allergy on nickel is inhibited by diamond powders.
Practical implications: Practical application metal implants with NCD in orthopedy, cardiosurgery, oral surgery, maxillo-facial surgery and dermatology.
Originality/value: We have observed anti-inflammatory, antiallergic and anticancerogenic responses from the carbon coatings layers onto medical implants like wires and screws.
Keywords: Nanomaterials; Nanocrystalline Diamond Coatings (NCD); Diamond Powder Particles (DPP); Biocompatibility

1. Introduction

Special unique properties like biotolerance and mechanical strength must be received to applay materials for implants. 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 [1].

2. Experimental

The aim of the study is in vitro and in vivo examinations of amorphous carbon coatings and medical applications obtained by the method of RF dense plasma CVD [1, 2]. The idea of RF dense plasma CVD method is to excite plasma in methane with nitrogen or other hydrocarbons with nitrogen in an RF electric field at a relatively high gas pressure of about hundreds of Pa. The substrate was coated with Nanocrystalline Diamond Coatings [1].

2.1. Examination

The carbon coated specimens have been tested to find their resistance to acids. Parameters of the examination have been described in previous publications [4].
A TEM microscopic image of carbon film deposited onto metal surface shows very small diamond crystallites [5] of grain size similar to this from an atomic force microscopy image [4].

A specificity of the layers, deposited by the method of dense plasma, consisting first of all in very good adhesion to steel is explained by the authors on the basis of investigations carried out by Auger electron spectroscopy (AES) [6] and microX-Ray Spectroscopy [3]. The carbon film passes smoothly into a thick layers (~micron) consisting of metal carbides of metals which are included in steel. Such a structure of the coatings ensures a higher mechanical strength [4].

In the bend test, the micrograph made by scanning electron microscope with such a substrate after 3 subsequent bending presents visible initial cracks. The micrograph of the same substrate after 10 bending presents a lot of cracks.

The corrosion tests have shown that the AISI 316L substrates with carbon coatings are unchanged, no corrosion products are visible. One of the parameters which make possible to state a coating applicability in medicine is the breakdown voltage in Tyrode's solution [3, 7]. Tyrode's solution is a water solution of salts which has the properties similar to that in human body. The value of the voltage allows us to estimate the corrosion resistance inside the human body. The breakdown voltage in Tyrode's solution for the uncoated steel oscillates between 340 and 420 mV mV. The applied coating should increase the value of the breakdown voltage to 1300 mV [3, 7].

2.2. Examination in vitro

Due to impossibility of in vitro test of carbon coatings in these examinations Diamond Powder Particles with extended surface have been used as the material. We have examined two types of diamond powder D1 - with diameter of 0.3-1.7 μm and D2 - with diameter of 0.2-1.8 μm: were manufactured by detonation method [9]. Erythrocytes (hematocrit of 1%) were exposed to 50 mM AAPH in phosphate-buffered saline at 310 K. To mixture of reaction were added the suspensions of D1 and D2 in amount $1x10^{-3}$g/$1x10^{-3}$l and after incubation at 310 K the time course of hemolysis was monitored by qualitative method and measurement of absorbance of hemoglobin in the supernatants at $\lambda = 414x10^{-9}$m after 0, 2, 3, 4 h [9].

2.3. Examination in vivo

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 [4].

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.

Results of preliminary histopathological investigations on laboratory animals were so promising (among others, there were no changes in the animals after several months) that attempts were made at implanting dental prosthesis in human [10].

2.4. Clinical research

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 (Figure 1) and Elocom. The method of patch test is described in [4].

Fig. 1. Procedure of preparation of patch test with diamond in human back skin

3. Discussion

The macroscopic observation of test aims shows that the surface of the uncoated steel is etched whereas the coated steel is intact. The observation by SEM confirms it. These tests confirmed the very good chemical inertia to aggressive liquid of the AISI 316 L steel coated with carbon by the RF PA CVD method and the possibility to use it for implants for surgery and other applications that need materials with good resistance to corrosion and chemical attack [4].

Additionally, 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 [4, 8]. 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 [11] and inhibits haemolysis in vitro examinations [4, 9]. 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 [12].

So far, carbon-coated implants have been used at many medical centres in Poland and abroad, such as those in Pabianice, Łódź (Poland) [13] and Liberec (Czech).

4. Applications of NCD coatings onto medical implants

4.1. Surgery implants

Due to positives all laboratory test next step is use as the carbon coatings coated implants in human body. Now has been made intensive research which consist in implanted into human body wires coated Nanocrystalline Diamond Coatings. First results are very optimistic and we are waiting for further examinations.

Second example is inserted screw or wires coated with carbon coatings into thigh bone [4] or brachial's bone (Figure 2) which don't demonstrate any influence on human body.

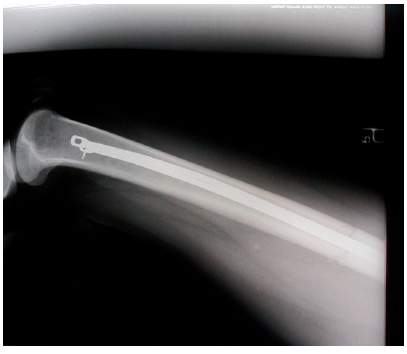

Fig. 2. X-ray picture of wire coated by Nanocrystalline Diamond coatings and implanted in human body

Schantz's screw which is presented on Figure 3 after 18 months in human body doesn't shown any influence on macro and molecular level on tissue. It is a prove that carbon coatings coating has been tolerated very well by body sites. Moreover, on the surface of the screw we can observe parts of tissue and it is a prove that this particles characterize high cohesion to the carbon coatings. Rescued of patient's leg is a special case confirm how important is deposited Nanocrystalline Diamond Coatings on implants what is impossibility using metal implants without carbon coatings.

Fig. 3. Screw coated by Nanocrystalline Diamond coatings after 18 months in human body

4.2. Tools for surgery

Another example are different tools for surgery with complicated shapes coated with adherent Nanocrystalline Diamond Coatings presented on Figure 4. It is very important in difficult sanitary conditions where is a lot of bacteria because on the carbon coatings surface doesn't occur any bacterial colonization what has been confirmed by Jakubowski et. al. [14].

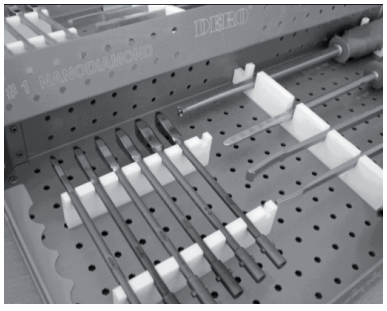

Fig. 4. An example of different tools for surgery

4.3. Antiallergic barrier diffusion

Samples coated with carbon coatings and implanted under human skin characterize biocompatible with contact allergy on molecular level (Figure 5). This phenomenon is explained following: Nanocrystalline Diamond Coatings is diffusion barrier which determine blockade diffuse of metal ionics into tissue [4]. Diamond powders (Figure 6) inhibit contact allergy on nickel in comparision with treatment by Elocom (Figure 5).

Fig. 5. The patch tests with DPP1 and DPP2 [9]

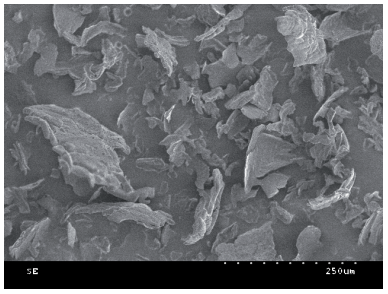

Fig. 6. SEM microscopic image of DPP synthetized with RF PACVD method

5. Conclusions

- Nanocrystalline Diamond Coatings is the biocompatible material which can be used in medicine onto medical implants and surgery tools.
- Nanocrystalline Diamond Coatings is the protection living organism between the metalosis, therefore different medical implants are covering with success by them. Carbon coatings is the barrier diffusion between implant and human environment confirmed in materials and biological tests.
- Nanocrystalline Diamond Coatings have not demonstrate any toxic reactions with living organism what have been proved in vivo and clinic tests.

References

[1] S. Mitura, K. Mitura, P. Niedzielski, P. Louda, V. Danilenko, Nanocrystalline Diamond, its synthesis, properties and applications, Journal of Achievements in Materials and Manufacturing Engineering, 16 (2006) 9-16.

[2] S. Mitura, E. Mitura, A. Mitura, Manufacture of amorphous carbon layers by r.f. dense plasma CVD, Diamond Relat. Mater., 4 (1995) 302-304.

[3] S. Mitura, A. Mitura, P. Niedzielski, P. Couvrat: Nanocrystalline Diamond, in, S. Mitura (Ed.); Nanotechnology in Materials Science, Elsevier, 2000.

[4] K. Mitura, P. Niedzielski, G. Bartosz, J. Moll, B. Walkowiak, Z. Pawłowska, P. Louda, M. Kieć-Świerczyńska, S. Mitura, Interactions between carbon coatings and tissue, Surf. Coat. Technol. (2006) in the press.

[5] S. Mitura, Proc. SPIE, Vol. 3179 (1997) 79.

[6] E. Mitura, A. Niedzielska, P. Niedzielski, L. Klimek, A. Rylski, S. Mitura, J. Moll, W. Pietrzykowski, The properties of carbon layers deposited onto titanium substrates, Diamond Relat. Mater., 5 (1996) 998-1001.

[7] E. Mitura, S. Mitura, P. Niedzielski, Z. Has, R. Wolowiec, A. Jakubowski, J. Szmidt, A. Sokolowska, P. Louda, J. Marciniak, B. Koczy, DLC coatings for biomedical applications Diamond Relat. Mater., 3 (1994) 896-898.

[8] S. Mitura, P. Niedzielski, D. Jachowicz, M. Langer, E. Tochitsky, P. Louda, P. Couvrat, M. Denis, P. Lourdin, Influence of carbon coatings origin on the properties important for biomedical application, Diamond Relat. Mater., 5 (1996) 1185-1188.

[9] K. Bakowicz, Bioaktywność diamentu, PhD Thesis, Politechnika Łódzka, 2003.

[10] P. Lourdin, P. Couvrat, M. Denis, S. Mitura, P. Niedzielski, J. Perrin, A. Koziarski, A. Olborska, Implants for dentistry coated by r.f. dense methane plasma, J. Chem. Vapor Deposit., 4 (3) (1996) 253-258.

[11] K. Bąkowicz, S. Mitura: Biocompatibility of NCD, J. Wide Bandgap Mater, 9 (4) (2002) 261.

[12] K. Mitura, G. Bartosz, S. Mitura, The inhibition of haemolysis in presence diamond powder particles in conditions of free radical damage, Engineering of Biomaterials, 43-44 (2005) 70-73.

[13] K. Zolynski, P. Witkowski, A. Kaluzny, Z. Has, P. Niedzielski, S. Mitura, Implants with hard carbon layers for application in, pseudoarthrosis femoris sin, ostisis post fracturam apertam olim factam, J. Chem. Vapor Deposit., 4 (3) (1996) 232-239.

[14] W. Jakubowski, G. Bartosz, P. Niedzielski, W. Szymanski, B. Walkowiak, Nanocrystalline diamond surface is resistant to bacterial colonization, Diamond Relat. Mater. 13 (2004) 1761-1763.