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Plasma modification of medical implants by carbon coatings depositions

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Materials

ABSTRACT

Purpose: The main goal was to work out the technology of deposition of carbon layers onto surface of medical implants made of the AISI316L medical steel. So far the results of carried investigations have proved that layers synthesized in RF PACVD process noticeably improve the biotolerance of the medical steel. Positive experimental results concerning the implementation of carbon layers conducted in the Institute of Materials Science and Engineering of the Technical University of Lodz were the basis for attempt of industrial application of the worked out technology.

Design/methodology/approach: Carbon layers were manufactured using radio frequency plasma RF PACVD method. The technology was worked out for the surfaces of the intramedullary nails. The investigations were carried out in order to compare obtained synthesis results with the layers deposited under the laboratory conditions. In this work the following are presented: the surface topography investigation, results of nanohardness and adhesion measurements as well as the raman spectra. Medical examination results were presented in our earlier publications. In the description of obtained investigation results are also presented the preliminary results of the medical treatment effects with the use of intramedullary nails covered with the carbon layer.

Findings: Carbon layers manufactured onto intramedullary nails presented good mechanical properties. Applied synthesis parameters made it possible to manufacture uniform film onto whole implant surface. Thickness of the layer was varied in the range of 200 – 400 nm, however total modification area contained 3.5 micrometers. Nails covered with the carbon layer positively passed the tests and were admitted into medical trade turnover. Positive medical treatment results were observed especially in case of patients with affirmed allergies onto alloying components contained in medical steels like chromium and nickel.

Research limitations/implications: Significant matter for the examinations had the introduction of the additional control parameters of the plasmo-chemical layers synthesis process. From the point of view of the industrial implementation of technology the fact of limited process efficiency can be.

Originality/value: The fundamental value of conducted investigations is the industrial application of the technology of deposition of carbon layers onto intramedullary nails. Currently those products are available in the business offer of MEDGAL Company.

Keywords: Nanomaterials; Biomaterials; Thin & thick coatings, Carbon coatings for medicine

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1. Introduction

Making a historical review of development of metallic materials used as implants one may state that there were attempts to apply a vast majority of metals and alloys which displayed a satisfactory biotolerance, resistance to corrosion and as well as the appropriate physico-chemical and mechanical properties. Long-lasting clinical trials provided one with the possibility of the assessment of their practical use. Based on this fact, the metals and alloys, which may be safely applied in surgery, with a small risk of side –effects, were singled out. Those materials were categorised as biomaterials.

To the present moment no biomaterial has been produced which could fulfil all the aforementioned requirements. All materials undergo biodegradation. It is essential that all products of degradation do not contribute to the negative effects such as toxic, mutagenic, cancerogenic effects and inflammation, and that there is a possibility of their removal from organism [1].

Metallic biomaterials still constitute basic materials used in the reconstruction of limbs. Clinical experiments with the application of those materials indicate that the actual level of mechanical properties ensures the possibility of their long-lasting use. The applied methods of analysis of tension and deformation in the systems: implant – bone – muscle enable to obtain an optimal choice of geometric characteristics of implants due to the biomechanical condition originating from the anatomic – physiological circumstances of the reconstructed bone system.

The investigations performed at present within the scope of biomaterial engineering focus on the problems concerning the enhancement of biocompatibility of the applied metallic materials by the application of methods of surface engineering. As it has been previously mentioned, the mechanical properties of metallic materials are satisfactory in the vast majority and they allow to produce the implants of good biomechanical characteristics, adjusted to the function performed. On the other hand, the possibility of the development of the corrosion processes and non-satisfactory tribological properties contribute to seek solutions aimed at their improvement. One of the ways of solving this problem is covering the implants or their elements with coatings of high biotolerance, for instance with carbon coatings.

It must be underlined that the authors of the publications concerning the investigations of the properties of carbon coatings in implantology are in agreement with the positive effect of those coatings on organism. It concerns both the enhancement of corrosion properties [2-4] and a decrease of the friction coefficient [5-6], the improvement of biocompatibility of an implant as well as the inhibition of the allergic reaction brought about unbeneficial influence of the material of the implant on organism [7-9]. Notwithstanding, it is still hard to find the examples of the industrial implementation of carbon coatings in implantology. It is indubitable that one of the reasons may be the technological obstacles with the technology transfer from the laboratory to industrial scale. Indeed, the plasma processes of synthesis of coatings are difficult to optimise and on the higher scale of production one encounters difficulties with their repeatability.

The aim of the study was to overcome the aforementioned problems and create the technology of production of nano-crystalline carbon coatings on the surface of medical implants.

2. Experimental

To synthesise a carbon layer the RFPACVD method was used. A device was equipped with a RF generator of power 2500 W, combined with an operating electrode through the system of power adjustment. The diameter of the RF electrode was 200 mm and the volume of a generator chamber was 80 dm^3. The method applied in the study and description of the device was defined in detail in the literature on the subject [10].

The object of synthesis was intramedullary nails. The material of the nails was medical steel AISI 316L. The technological process was developed for the whole range of nail dimensions which are within the length from 150 to 520 mm and diameter from 8 to 13 mm. The nails were located in the working chamber on the specially prepared handles ensuring the uniform distribution of plasma field on the whole surface.

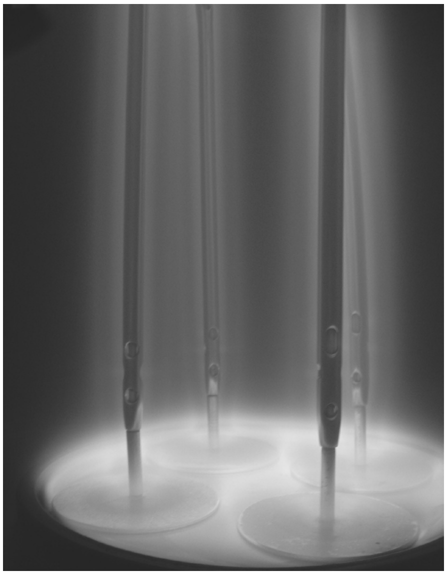

Fig. 1. View of nails during carbon coating deposition using RF PACVD method

The operating atmosphere in the course of the process was methane. The process of the synthesis comprised two stages. The objective of the first stage was pre-heating and making uniform the temperature on the coated elements. It was performed at the pressure 10 Pa and negative electrode potential -1000V. The second stage was aimed at the production of the coating and was carried out at the pressure of 50Pa and polarisation of the electrode -800V. The total time of the process from the moment of insertion to removal of the implants from the chamber was from 30 to 40 minutes. The view of implants during carbon coating deposition using RF PACVD method is presented in Fig.1.

3. Results

The encouragement to attempt the industrialization of the aforementioned technology was the previous investigations of their mechanical and biological properties. They proved that the mechanical properties such as adhesion, hardness, resistance to abrasion are sufficient to ensure the stability of the layer in the course of utilisation of the implant. Furthermore, high biotolerance, chemical and corrosion resistance were confirmed [10].

The investigations presented in this section were aimed at the confirmation of the previously obtained results concerning a finished medical product. This necessity is connected with the specificity of RF PACVD plasma processes used to the coatings synthesis. A relevant meaning for the properties of the obtained layer is not only the stability of the process and parameters of production but also the size and shape of the modified elements.

The layers are characterised by the homogeneity and uniformity of the coating on the whole implant surface. The AFM investigations indicate that the coating structure is typical for the nanocrystalline layers and the results obtained by Raman spectroscopy indicate that the layer is of the DLC type with peaks: D (1360 cm^{-1}) and G (1610 cm^{-1}). To define the mechanical properties of the surface NanoIntender G200 was applied. The nano-hardness of the layer surface was established on the level 13 GPA (Fig. 2), the Young's modulus – 230 GPa and the critical adhesion force was equal to 50 mN (Fig. 3).

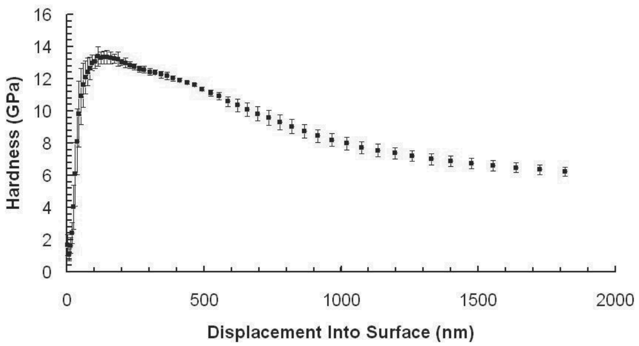

Fig. 2. Friction coefficient as a function of load applied on the sample for carbon coatings deposited on medical steel AISI 316L

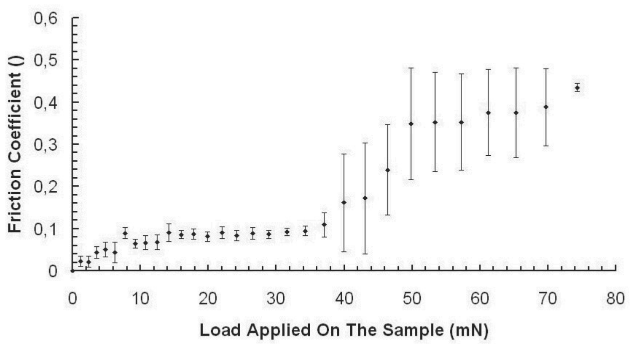

Fig. 3. Cross-section of carbon layer deposited on medical steel AISI 316L with a visible inter layer

The satisfactory mechanical properties are connected with a diffusion character of the layer. The total thickness of surface modification is equal to 3.5 micrometers, out of which 200 to 400 nm is comprised of carbon layer and the rest is the interface (Fig. 4). The structure of the interface is markedly different from the original structure of the material. It may be defined as an area of the grinded grains of austenite with the release of metal carbides. The process is carried out in such a way as not to allow to release the chromium carbide, which is responsible for intra-crystalline corrosion. The process is regulated by maintaining the temperature of the covered elements on the level of 480 – 500 ºC. Such a temperature in the plasma process is sufficient to evoke the occurrence of diffusion of carbon but it does not allow to release chromium carbides.

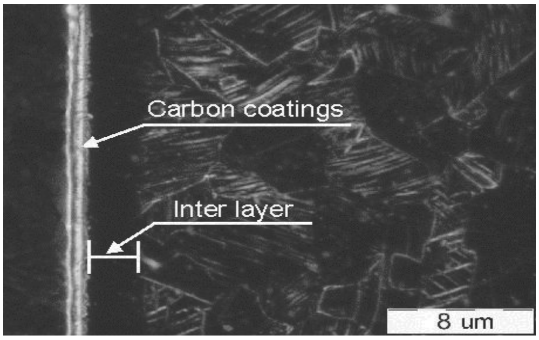

Fig. 4. The X-ray photos of the treatment of broken bone using nails with a carbon layer

4. Discussion

Among the reactions of human organism to metal implant, a key role is played by the reaction of immune system as a physiological response of the organism to foreign substances. Nevertheless, in certain cases the immunological response may change into illness such as allergy. To allergens one may account metallic implants, such as nickel, cobalt, chromium, iron and the others. Allergy and reaction around the implant occur when there is a contact between the tissues of the organism with metal and its salts. According to the authors, it is assumed that from 6% to 33% of population suffer from allergy to nickel; from 7% to 11% suffer from allergy to chromium [11-14]. Most of the statistics concern allergy to implants made of stainless steel [15, 16], though many of the statistics report the allergy to alloys comprising cobalt and chromium [14, 16]. In certain non-documented cases the allergic processes led to the necessity to remove implants [17]. Sometimes, one may observe the inflammatory processes. Other investigations confirmed that the elements released by the alloys like chromium, nickel and cobalt may be cytotoxic [18].

The former examinations proved that carbon coating may constitute a barrier to metal ions. This limits to a large extent an amount of metal ions moving from the implant to the organism. This phenomenon minimises the risk of incidence of allergic complications. Such investigations were carried out by K. Mitura, among others on a group of patients with the confirmed allergy to Cr, Ni and Co [19].

The equally positive results were obtained in the examinations under consideration. The inclusion criteria concerning the treatment using the implants with carbon coatings encompassed the patients with the confirmed allergy to metal ions. The observations of the course of treatment gave the similar results in all cases. The appropriate and quick healing of a post-operation wound was confirmed. In the whole course of treatment lasting about one year, a lack of allergic and inflammatory reactions and smaller pain were observed. In the completed cases of treatment there were carried out the investigations of the state of the surface of nails after a period of time spent in the organism of a patient. The only alterations of the surface of implants resulted from the mechanical damage during nails removal from organism of the patient. Analogously, in the samples of tissue from the area of implant taken from patients, changes indicating the occurrence of cytotoxic, inflammatory or allergic reactions were not noticed. An example of X-ray photos of the treatment of a broken bone using nails with a carbon layer is presented in Fig. 5.

Fig. 5. The X-ray photos of the treatment of a broken bone using nails with a carbon layer

5. Conclusions

The investigations presented in this paper were aimed at the formation of carbon coating on the surface of metal implants, in this case the nails. The basic problem was to obtain the coating of similar properties as the coatings formerly obtained on the laboratory tested samples on the finished medical product. The prerequisite to success was to stabilise the parameters of the synthesis of the coating and achieve the full repeatability of the process. To reach that goal it was relevant to define the appropriate parameters of the synthesis, adjusted to the dimensions of the modified elements and their influence on the quality of the obtained coating. The essential parameter was to properly place the implants in the chemical-plasma chamber. This location influenced the uniform distribution of plasma field on the whole modified surface, which allowed to obtain a homogenous coating. The appropriate mechanical and biological properties of the system: carbon coating – the implant were confirmed in the laboratory tests and clinical practice. In the case of the modification of the surface of nails, the formation of tight diffusion barrier between the metal of the implant and the organism of the patient was regarded as the greatest achievement. The layer, to a large extent, contributes to a decrease in penetration of metal ions to the organism, protecting the patient from an incidence of complications due to allergy. This ensured enhancement of biocompatibility of the implant and reduced the risk of an incidence of complications in the course of treatment, in particular in the case of people suffering from the oversensitivity to metal ions.

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