

Diamond biocompatible coatings for medical implants

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New carbon (diamond-like) nanocomposite coatings deposited from a C_{60} ionic beam can be used as a wear-resistant protective coating for implants. It was found that these coatings enhance resistance to electrochemical corrosion processes due to a shift of the material's electrode potential to a zone of positive values. They also promote a complex of reparative, adaptative and compensatory reorganization that accelerates the healing processes in the vicinity of the implant.

Keywords: biocompatibility, diamond-like films, electrode potential, implant coating, nanocomposite, structure

1. INTRODUCTION

The selection of material for the manufacture of medical implants has always betokened a certain complexity. Most metals have either insufficient chemical inertness or inadequate mechanical properties for the job [1, 2]. One solution to the problem is to apply carbon coatings of broad functionality to metal implants that fulfil all mechanical requirements [3]; in particular diamond-like carbon coatings. Such coatings possess unique mechanical, chemical and thermal characteristics. The combination of low friction and high wear resistance gives enhanced durability; for example, when artificial joints are formed [4]. Furthermore, diamond-like carbon (DLC) coatings exhibit excellent biocompatibility, in contrast to other types of coatings that cause blood coagulation, and are effective barriers preventing diffusion of metal ions, hence they can be effectively used for implants in contact with bone [5].

The validity of using of carbon film as a coating for prostheses and implants depends on the ability of carbon materials to quickly become assimilated with the surrounding tissues, as well as stimulate the formation of new bone, together with good biochemical compatibility. Moreover, carbon materials possess the attribute of biostimulatory power, promoting regeneration of the tissues surrounding the implant. Products of wear or failure, being carbonaceous, do not adversely affect the surrounding tissue and lymph nodes, nor the organism as a whole. Thus, these materials are very promising for use as implant coatings.

Diamond-like coatings can be deposited on various types of substrates using methods such as spraying [6], pulsed laser deposition [7] or ion beam deposition [8]. Unlike other techniques, the ion beam deposition of

fullerene C_{60} , instead of atomic carbon, provides a new diamond-like material having a unique nanocomposite structure and a low level of residual stress [9]. The synthesized film consists of graphite nanocrystals embedded in an amorphous diamond-like matrix. The graphite nanocrystals have a preferred orientation of the graphene planes (perpendicular to the surface). This structure led to a high ratio of hardness to Young's modulus, which made it possible to expect the best combination of mechanical properties of both coating and metal substrate, in comparison with diamond-like coatings made by conventional methods using an atomic carbon beam. The preferential orientation of the graphite nanocrystals plays an important rôle in the transition from biocompatibility to more biological activity of the coatings, since there is a difference in the chemical and biochemical properties of graphite crystals depending on the crystallographic direction [10].

This new type of diamond-like nanocomposite coating has its own topography [9] in addition to excellent mechanical and tribological properties. Such nanoscale topography can be useful for various biological applications.

The study of biocompatibility of carbon nanocomposite coatings formed by an ion beam of C_{60} should lead to the development of a new class of carbon coatings having optimal mechanical properties. The purpose of the study was to determine the electrochemical activity and biocompatibility of such coatings deposited on a cobalt–chromium alloy in comparison with uncoated cobalt–chromium alloy and titanium.

2. EXPERIMENTAL

Two types of metal alloys were used for sample preparation: the cobalt–chromium alloy Vitallium (Co 62%, Cr 30%, Mo 5%, C 0.4%) and the titanium alloy

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VT1-0 (Ti 99%, Fe 0.18%). Plates with dimensions of $10 \times 15 \times 2$ mm were prepared. Fullerene C_{60} powder (99.5% purity; NeoTechProducts, St Petersburg, Russia) was used as the source material for the deposition of the carbon nanocomposite coatings.

Carbon nanocomposite coatings were deposited onto Co–Cr alloy plates by a C_{60} ion beam with average ion energy of 5 keV. The deposition was carried out in a modified vacuum setup (VUP-5M, Selmi, Ukraine) equipped with liquid nitrogen traps. The base pressure was 10^{-4} Pa, and the pressure of Ar during the deposition was 5×10^{-3} Pa. Two oppositely directed ion beams were formed from the ion source with a saddle-shaped electric field. The first beam was used for monitoring and the second one for deposition. C_{60} vapour was supplied from two effusion cells through a channel in the anode directly to the saddle point of the electric field. Ar with a purity of 99.99% was supplied to the cathode via an SNA-2 supply system (Selmi, Ukraine). The temperature of the substrate was 100 °C.

Prior to loading the fullerene into the effusion cells, the cells were cleaned by vacuum distillation. Before deposition, the loaded effusion cells were maintained under high vacuum (2×10^{-4} Pa) at a temperature of 300 °C for 3 h. For the deposition of uniform coatings over a large area, the substrates were mounted onto a holder that reciprocated across the ion beam in two directions. Film deposition rate was 0.1 nm per second, the thickness of the films was 20–100 nm [11].

DLC coating structure was examined with transmission electron microscope TEM-125K at a resolution of 0.2 nm. Samples were prepared on NaCl substrates. After separating the films from their substrate they were washed with deionized water and placed on a copper grid.

Electrode potentials were measured in an electrochemical cell filled with an 0.9% aqueous solution of NaCl using a standard AgCl reference electrode [1] for rating initial activity of the metals.

Biological estimation of coating integration required animal experiments. Rabbits (20 months old with body mass of approximately 3 kg) were separated into three groups. Subperiosteal implants made of Co–Cr alloy, titanium alloy and nanocomposite-coated Co–Cr alloy were implanted in rabbits from the first, second and third groups, respectively. Rabbits were sacrificed by air embolism at 12 weeks.¹

After the rabbits were sacrificed, a fragment of the mandible, including the implant and a portion of the adjacent bone comprising an outer and an inner compact bone and spongy substance, was extracted. The

extracted material was visually examined using an optical microscope (Leika Axiostar Plus), for which the extracted fragments were fixed in 5 vol.% nitric acid, then dehydrated in 96% ethanol and embedded into celloidin [12]. Cross-sections with thicknesses of 7–10 μ m were coloured with haematoxylin, eosin and van Gieson's stain.

Morphometric investigations concentrated on the following characteristics: an estimation of the newly formed tissue between the parent compact bone and the implant; the presence of necrosis on the surface of the tissue adjacent to the implant; and assessment of the nature of the restructuring of the compact and trabecular bone [13].

3. RESULTS AND DISCUSSION

Transmission electron microscopy of the carbon nanocomposite coatings revealed the contrast inherent to amorphous films, and microdiffraction consisting of two halos with peaks characteristic of amorphous carbon (Fig. 1). The changes of structure, mechanical, electrical and optical properties of such coatings at different substrate temperatures during deposition are described in [11]. These coatings have high values of the moduli of elasticity (340 GPa) and hardness (46 GPa).

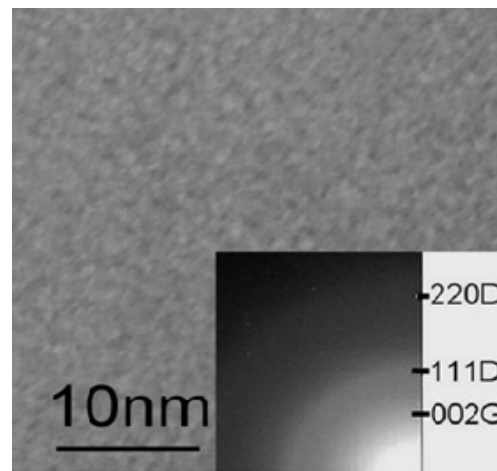


Figure 1. Micrograph and electron diffraction pattern of diamond-like nanocomposite film. The positions corresponding to the family of graphite (G) and diamond (D) planes are marked on the electron diffraction pattern.

Time dependencies of electrode potentials of all three samples types are presented in Fig. 2. The duration of measurements was that required to achieve a constant potential. The Co–Cr alloy gave the lowest potential; at the beginning was -0.32 V and, after slight growth and stabilization, it arrived at -0.15 V. The electrode potential

¹ The animal tests were performed according to the requirements of the European Convention and Ukrainian law.

of titanium was practically unchanged during measurement (0.05 V). The Co/Cr alloy with DLC coating had the greatest electrode potential (0.2 V) and hence maximum initial resistance to electrochemical corrosion.

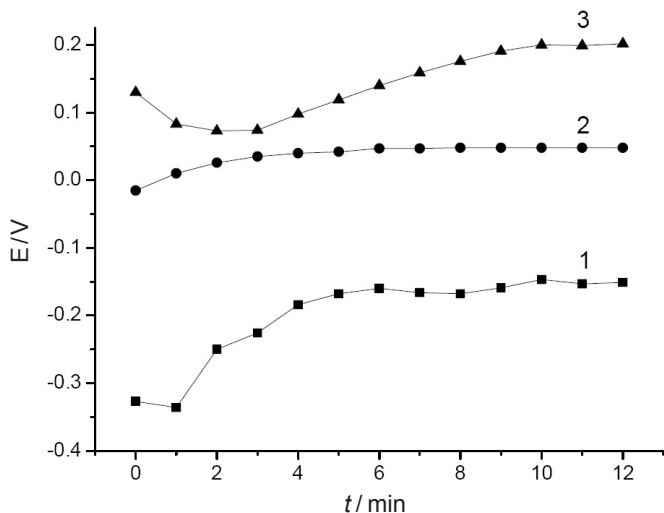


Figure 2. Time dependence of electrode potential for Co–Cr implant (1), Ti implant (2), and Co–Cr implant with carbon diamond-like nanocomposite coating (3).

Figure 3 shows the contact zones of bone and implants made from Co–Cr alloy, titanium, and Co–Cr alloy with the nanocomposite DLC coating three months after surgery.

Microscopic investigation revealed that the Co–Cr alloy implant firmly adhered to the surface of the bone and was partially covered by connective tissue. Connective tissue sections with a high density of fibroblasts were observed in the areas between the implant and compact jaw bone (Fig. 3a). At other locations, the implant was in direct contact with the parent bone. In these areas the bone tissue had signs of destructive disorders, such as absence of osteocytes, presence of demineralization centres, and chaotic arrangement of basophilic gluing lines. The small centres of cellular detritus are found as compact bone restructuring areas with small resorption cavities. These cavities were filled with friable connective tissue. The centres of bone remodeling with narrow basophilic gluing lines and deposition of bone tissues between them were also observed. The morphological parameters of the mandible after implantation of the Co–Cr alloy plates are shown in Table 1.

The microscopic investigation of compact bone sites adjacent to the Ti alloy implant revealed zones of newly formed mature bone, along with connective tissue, a low density of fibroblasts and bundles of collagen fibres (Fig. 3b). Isolated foci of necrosis between the implant

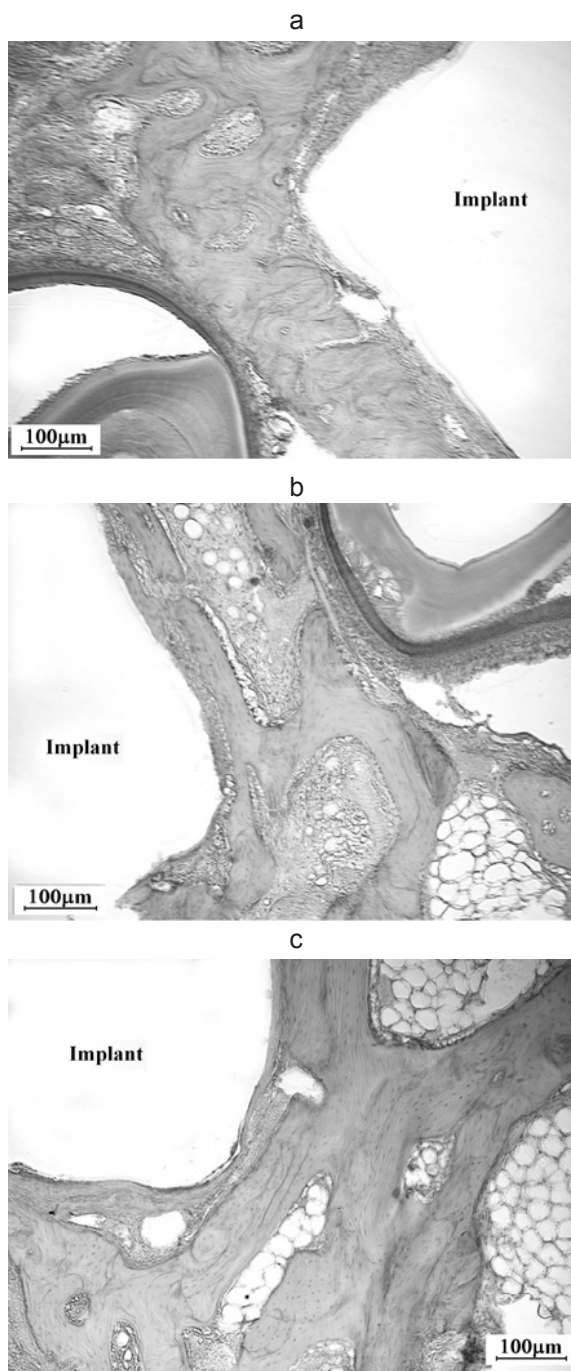


Figure 3. Microscopy of contact zones of implants and bone: a, Co–Cr implant; b, Ti implant; c, Co–Cr implant with carbon diamond-like nanocomposite coating.

and the newly formed tissue were observed. Evidence of restructuring processes was observed in the compact bone of the jaw near the surface of the implant. These processes required the formation of resorption cavities, which were filled with friable connective tissue with a high density of capillary-type blood vessels. The density of osteoblasts was increased in the edge regions of trabecula of the cancellous bone. Intertrabecular spaces were also filled with friable connective tissue.

Table 1. Severity of morphological parameters of the mandible body for animals 12 weeks after implantation.

Indicator	Parameter	Implant type		
		Co–Cr alloy	Titanium alloy	Co–Cr with DLC coating
Newly formed tissue between parent compact bone and implant	Connective tissue (%)	89.7±0.9	76.3±4.3	69.3±4.8
	Coarse-fibred bone (%)	10.3±0.9	23.7±4.4	31.7±1.8
Foci of necrosis at the tissue surface adjacent to the implant	Absence			yes
	Isolated foci	yes	yes	
	1/3 of the contact surface			
Nature of the compact bone restructuring	Osteocyte-free area (%)	33	33	25
	Resorption cavity (%)	50.70±2.60	44.67±2.60	41.67±3.33
	Deminerlization foci	single	single	absent
Characteristics of trabecular bone reconstruction	Density of osteocytes	119.3±1.2	122.0±6.4	158.0±1.2
	Expanded intertrabecular space (%)	61.0±4.4	57.3±4.4	43.7±2.6

The microscopic investigation of Co–Cr alloy with the nanocomposite DLC coating showed that edge surfaces of the implant were covered with connective tissue. Areas with rough bone were primarily observed between the implant and the compact body of the jawbone. Only small areas containing connective tissues with collagen fibres arranged parallel to the surface of the implant were evident. Only single, mature fibroblasts were observed (Fig. 3c). Resorption cavities were observed on compact bone areas located under the implant. These cavities had various shapes and sizes and were filled with friable connective tissue or bone marrow fat. Some signs of restructuring, which included the formation of basophilic gluing lines, were observed. These gluing lines separated the generation of deposition and the neogenic bone tissue. These areas contained a high density of osteoblasts (Table 1).

Thus, comparative analysis of bone reconstruction after the fixation of implants of various materials to the compact bone of the mandible has revealed that in all cases after implantation, complex reparative and compensatory–adaptive restructuring, the severity of which depends on the implant material, occurs in compact and trabecular bone. It was revealed that in terms of newly formed tissue between parent compact bone and implant, the most favourable results were observed for the implant made of Co–Cr alloy with nanocomposite DLC coatings. In this case it was observed that maximal formation of coarse fibre bone and minimal presence of connective tissue, as well as more favourable values of other parameters, obtains. The average position was held by the implant made of titanium, while more pronounced unfavourable rates were monitored for the Co–Cr implant without coating.

4. CONCLUSIONS

The experimental results showed that the deposition of carbon nanocomposite DLC on a Co–Cr alloy increases the biological compatibility of the implant, reducing the risk of fibrous tissue formation near the implant surface, hence increasing the initial stability and durability of the implant. This coating improves the resistance of the implant to electrochemical corrosion processes due to a shift of its electrode potential to positive values. In terms of physiological effect, the influence of coating is determined by the behaviour of complex reparative and adaptive–compensatory restructuring that can accelerate the healing process and postoperative adaptation of the body in the implant fixing zone.

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