Biomaterials 102 (2016) 130–136

Contents lists available at ScienceDirect

Biomaterials

journal homepage: www.elsevier.com/locate/biomaterials

Highly wear-resistant and biocompatible carbon nanocomposite coatings for dental implants

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A R T I C L E I N F O

Article history:
Received 8 April 2016
Received in revised form
10 June 2016
Accepted 11 June 2016
Available online 15 June 2016

Keywords:
Carbon nanocomposite
Biocompatibility
Wear resistance
Dental implants
In vivo

A B S T R A C T

Diamond-like carbon coatings are increasingly used as wear-protective coatings for dental implants, artificial joints, etc. Despite their advantages, they may have several weak points such as high internal stress, poor adhesive properties or high sensitivity to ambient conditions. These weak points could be overcome in the case of a new carbon nanocomposite coating (CNC) deposited by using a C_{60} ion beam on a Co/Cr alloy. The structure of the coatings was investigated by Raman and XPS spectroscopy. The wear resistance was assessed by using a reciprocating tribotester under the loads up to 0.4 N in both dry and wet sliding conditions. Biocompatibility of the dental implants was tested *in vivo* on rabbits. Biocompatibility, bioactivity and mechanical durability of the CNC deposited on a Co/Cr alloy were investigated and compared with those of bulk Co/Cr and Ti alloys. The wear resistance of the CNC was found to be 250–650 fold higher compared to the Co/Cr and Ti alloys. Also, the CNC demonstrated much better biological properties with respect to formation of new tissues and absence of negative morphological parameters such as necrosis and demineralization. Development of the CNC is expected to aid in significant improvement of lifetime and quality of implants for dental applications.

1. Introduction

The proper selection of an implant material is usually a complicated process because the biocompatibility must be assured together with sufficient durability and manufacturability of the material. Most commonly used metals exhibit low chemical passivity resulting in low biocompatibility and high corrosion of the surface [1–6]. Use of relatively passive ceramics is also limited because of their high brittleness [7]. These chemical and physical limitations lead to an increase in the thickness and geometrical dimensions of implants. It has been suggested that such issues may be overcome by development of appropriate composite materials [8–14]. However, the use of composite materials in implants introduces new challenges. A composite, while in contact with bone tissue, should exhibit high delamination stability, high adhesion and uniform contact [9–16]. Additionally, the coating and the substrate materials of an implant should have similar mechanical and physical properties such as thermal expansion coefficient and Young's modulus.

Development of carbon-based functional coatings for biomedical applications has been gaining increasing attention over the recent years. The use of carbon-based composites has significantly increased the wear resistance of implants [17–19]. Also, diamond-like carbon (DLC) coatings have recently received much attention because of their unique mechanical, chemical and thermal characteristics [20,21]. The combination of low friction and high wear resistant properties of DLC has increased the durability of precision components and friction pairs such as artificial joints [22]. Also, metallic implants with DLC coatings have demonstrated high biocompatibility [17,22]. Unlike other coating materials, DLC does not lead to blood coagulation. Instead, it effectively blocks the diffusion of metal ions, and therefore, it may be used to coat implants in contact with bone or soft tissues of the body. In fact,

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http://dx.doi.org/10.1016/j.biomaterials.2016.06.029
0142-9612/

carbon-based materials have demonstrated the ability to coalesce with surrounding tissues and to stimulate bone formation [23].

Non-hydrogenated DLC coatings can be deposited on different substrates by various methods, including sputtering [24], pulsed-laser deposition [25] or ion-beam deposition [26]. Each method has its own advantages as well as disadvantages such as high levels of internal stress, poor adhesive properties or high sensitivity to ambient conditions. These disadvantages of DLC coatings could be successfully overcome by using an accelerated fullerene ion beam during the deposition of carbon nanocomposite coatings (CNCs) [27–31]. The ion-beam deposition by using C_{60} fullerene molecules (instead of atomic carbon) allowed the formation of a new carbon-based material with unique nanocomposite structure and low level of internal stress [27,28], high adhesion to substrate [27] and low amount of defects [31]. The microstructure of CNC consisted of graphite nanocrystals embedded into an amorphous diamond-like matrix [29]. The graphite nanocrystals had a well-defined preferential orientation of graphene planes that were perpendicular to the surface [28]. It has been reported that the preferential orientation of the graphite nanocrystals plays an important role in the transition from biocompatibility of the coatings to their bioactivity, because of the sufficient difference in chemical and biochemical properties between the base and the edge directions of graphite crystals [32]. The nanocomposite structure also showed a relatively high ratio of hardness to Young's modulus, which led to better matching between the mechanical properties of the coating and a metallic substrate compared to DLC coatings deposited by traditional methods. Besides, thin DLC coatings usually have smooth surface and tend to reproduce the initial topography of the substrate [17]. CNCs deposited by the C_{60} ion beam showed unique nanoscale topography [29,30] that could be helpful for various biological applications [33,34].

For a number of reasons mentioned above, the CNC deposited by using a C_{60} ion beam could lead to the development of a new class of carbon coatings with excellent mechanical properties and biocompatibility. In this study, the most important requirements of a dental implant such as biocompatibility, bioactivity and wear resistance of the carbon nanocomposite coated on a Co/Cr alloy by C_{60} ion beam deposition technique were investigated and compared with those of bulk Co/Cr and Ti alloys. Methods used for specimen fabrication and experimental details are described in the following sections.

2. Materials and methods

2.1. Materials

Two types of metal alloys were used for preparation of the specimens: cobalt-chromium alloy, Vitallium (Co 62%, Cr 30%, Mo 5%, and C 0.4%) and titanium alloy, VT1-0 (Ti 99% and Fe 0.25%). Metallic plates with dimensions of $10 \times 15 \times 2$ mm^3 were used. C_{60}–fullerene powder (99.5% purity; NeoTechProducts, St. Petersburg, Russia) was used as the source material for the deposition of the CNCs.

2.2. Specimen preparation

CNCs were deposited on Co/Cr alloy plates by a C_{60} ion beam with an average ion energy of 7.5 keV. The deposition was performed in a modified vacuum setup (VUP-5M, Selmi, Ukraine) equipped with liquid-nitrogen traps. The base pressure was $1 \cdot 10^{-4}$ Pa, and the pressure of Ar during the deposition was $5 \cdot 10^{-3}$ Pa. Two oppositely directed ion beams were formed at the ion source with a saddle-shaped electric field. The first beam was used for monitoring and the second one was used for deposition. C_{60} vapor was supplied from two effusion cells, through a channel in the anode, directly to the saddle point of the electric field. The substrate temperature during the deposition was 250 °C.

Prior to loading the fullerene powders into the effusion cells, they were cleaned by vacuum distillation. Before the deposition, the loaded effusion cells were maintained under a high vacuum ($2 \cdot 10^{-4}$ Pa) at a temperature of 300 °C for 3 h. The temperature of the effusion cells during deposition was above 500 °C. For deposition of uniform coatings over a large area, the substrates were mounted on a holder that reciprocated back and forth across the ion beam. More detailed descriptions of the deposition process are available elsewhere [35,27].

2.3. Coating characterization

The structure and chemical composition of the coatings were investigated using scanning electron microscopy (SEM; Jeol 6210) in conjunction with energy-dispersive X-ray spectroscopy (OXFORD INCA Energy), Raman spectroscopy (LabRam Aramis) conducted at a wavelength of 532 nm, and X-ray photoelectron spectroscopy (XPS; Thermo Scientific K-Alpha). The thickness measurements were performed after deposition of the coating using a step method. Electrode potentials were measured using the standard AgCl electrode for rating the initial activity of metals [3]. The measurements were conducted in an electrochemical cell filled with physiological fluid (0.9% aqueous solution of NaCl). A standard AgCl reference electrode was used.

2.4. Friction and wear testing

A commercial reciprocating tribo-tester (CETR UMT-2) was used to investigate the wear behavior of the coating in both dry and wet sliding conditions. Artificial saliva (Xerostomia Saliva; Kalmar) was used as a media for the wet conditions. It should be noted that artificial saliva is commonly used for simulation of the actual biological environment in various dental experiments [36]. All experiments were performed under ambient temperature of approximately 25 °C and relative humidity of 45–55% in a Class 100 clean room. The sliding speed was set to 4 mm/s with a stroke of 2 mm, which corresponded to a sliding frequency of 1 Hz. Alumina balls with a diameter of 1 mm were chosen as the pins because of their high hardness and good chemical stability. An accelerated wear testing method was used to shorten the experiment time [37]. Thus, the loading conditions were selected to be much more severe compared to the actual biological environment. The normal load was set to either 50 mN or 400 mN, depending on the wear resistivity of the specimens. The corresponding maximum contact pressure was estimated using the Hertzian equation [38]. The repeatability of the experimental data was ensured by performing the sliding tests at least three times for each set of experimental conditions. A new pin was used for each experiment.

After the sliding tests, the amount of wear was assessed using a 3D laser microscope. The cross-sectional profiles of the wear tracks were mapped using a laser beam at a wavelength of 408 nm. The laser beam precisely scanned the specimen at a frame rate of 9 Hz with a high resolution of 1024×768 pixels. The normalized wear rate was then calculated by dividing the wear volume by the number of sliding cycles and the applied normal load.

2.5. Biocompatibility evaluation

Rabbits (20 months old with a body mass of approximately 3 kg) were separated into three groups for biocompatibility evaluation. Subperiosteal implants made of Co/Cr alloy, titanium alloy and nanocomposite-coated Co/Cr alloy were implanted in rabbits from