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Nanotribology of silver and silicon doped carbon coatings

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ABSTRACT

Amorphous hydrogenated carbon coatings a-C:H become very popular materials mainly because of their excellent properties such as low coefficient of friction, high hardness, good anti-wear and corrosion properties. More and more often are carried works aimed at improvement of biocompatibility and adhesion of bacterial cells by doping diamond-like carbon (DLC) coating with third element. Among them recently a great majority is devoted to carbon coatings doped with silver or silicon. The presence of silver in the coating ensures protection of the implant against the disadvantageous influence of bacteria and fungi causing biofilm associated infections, local inflammation and other implant-tissue reactions. Incorporation of silicon promotes osteointegration and leads to the enhancement of mechanical and tribological properties of the coating, which is beneficial for biomedical applications.

Silver and silicon incorporated DLC coatings were prepared by a hybrid Radio Frequency Plasma Assisted Chemical Vapor Deposition/Magnetron Sputtering deposition technique on AISI316L substrates. Obtained coatings were characterized in terms of morphology, surface topography and mechanical properties. Tribological properties of the coatings were measured by lateral force microscopy and reciprocating sliding test using nanoindenter.

1. Introduction

The number of hip and knee joint prosthesis implanted annually in England and Wales increased from approximately 109,825 to 166,000 only within the period of two years (2008–2010). This is due to prolongation of human life, improvement of medical services and frequent qualification for implantation of younger people [1]. Biomaterials used for medical implants should meet three conditions: do not cause side reactions in the form of allergies or inflammation, should be characterized by hemocompatibility as well as optimal mechanical properties depending on the target (implanting site) [2]. In consequence, the most common are the systems resulting from the combination of two materials with very different physical and chemical properties. One of these materials (the core) replaces a lost anatomical structure or function and e.g. transmits forces due to biomechanics of movement. The second is the coating material that fulfills a specific function (functional material). It protects the core against the influence of the tissue environment on the implant and consequently protects tissues against the metal ions released from the bulk material. It is usually characterized by improved mechanical properties and lower coefficient of friction in friction pairs (joints). The coating material may have anti-bacterial properties and the ones resulting in better integration with the surrounding tissue (osseointegration) [2–5]. For the surface modification of biomaterials variety of plasma methods is used, e.g. glow discharge, electron cyclotron resonance, corona discharge, atmospheric plasma processes, physical and chemical vapor deposition, plasma polymerization, grafting for polymeric surfaces and plasma spraying [4]. One of the possible surface modification of the materials including biomaterials is the synthesis of thin coatings. Among many types of coatings which are synthesized by few of the techniques mentioned above are carbon films. The best known allotropic forms of carbon are graphite and diamond. Carbon exists also in the form of nanotubes, fullerenes and increasingly popular graphene [6] which involves very high applications hopes mostly because of its properties which are unachievable to other materials [7,8]. In the broadly understood engineering applications together with these related to biomaterials the most frequently used carbon layers are these of disordered network of carbon atoms with sp^2 and sp^3 electron hybridizations. Such coatings are commonly described as diamond-like (DLC). Amorphous hydrogen-free (a-C) or hydrogenated (a-C:H) carbon coatings unmodified or doped with different elements are used as the protective anti-wear coatings in the automotive industry. Properties that make them so attractive for various applications include high hardness, chemical inertness, optical properties, biocompatibility, resistance to corrosion and excellent tribological properties - which pretend it for use in frictional associations [6]. A major drawback of DLC coatings is their poor adhesion to the substrate. This is due to stress in the layer resulting from the process of synthesis and the structure of amorphous carbon coatings. This problem, however may be overcome by the application of an adhesion promoting interlayer. As the intermediate coatings CrC, Si_3N_4 [1] or Ti [1,9] are used. Similar results can be achieved by the incorporation of different elements to DLC coatings like Cr, Ti, W as well as Ag and Si. Wang et al. [10] showed that incorporation of c.a. 10 at.% of silver increases the hardness of DLC

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coatings from 25 to 35.2 GPa, however, for higher Ag contents the hardness values decreased. Together with doping DLC with silver decrease of the residual stress and a twofold increase in the delamination force in the scratch test method occurs [11]. Endrino et al. [12] presented an increase in hardness of Ag incorporated a-C coatings and slight decrease of this parameter for a-C:H layers. However, more reports regarding the opposite behavior of Ag-incorporated DLC, where the incorporation of Ag resulted in the reduction of the hardness, can be found in literature [13–16]. Batory et al. [17] showed that mechanical parameters of silver implanted DLC are rather insensitive to different doses of silver ions (with energy of 15 keV), and at the same time surface concentrations of silver (at least to 4 at.% of Ag). A positive influence of the dopant can be also observed for DLC coatings with addition of silicon (5 at.%) [18]. The studies of Ikeyama, Bendavid and Papakonstantinou [19–21] revealed that increase of the silicon concentration in the coating causes decrease in hardness, elasticity modulus as well as the residual stress in the coatings which positively influence the adhesion. Silicon is also known to decrease the coefficient of friction. Hofmann et al. [22] in their work presented slight increase in the hardness of silicon doped DLC coatings. Simultaneously with increasing silicon content in the coating the hydrogen content decreased and increase in abrasive wear was noticed. In contrast Wang et al. [23] reported noticeable increase in hardness of Si-DLC coating from 7 GPa for unmodified DLC to 22 GPa for concentration of 14.8 at.% of silicon. This coating also presented the lowest wear and friction coefficient. Doping DLC with elements such as Si and Ag in addition to improved mechanical properties and adhesion entails specific biological properties. In the in vivo tests it was shown that addition of silicon promotes the adhesion and proliferation of osteoblasts [20] as well as it may limit the adhesion of microorganisms to the surface [24]. Similarly, the incorporation of silver provides the bacteriostatic properties, however the analyzed surfaces exhibit also a good hemocompatibility [25,26].

In the presented work the nanotribological properties of Si and Ag incorporated a-C:H coatings together with the influence of the concentration of the dopant on the morphology and topography of obtained coatings are examined. The applied coatings and the dopants were chosen based on the literature review and our own experience [27,28] with regard to their potential application in medicine as the protective coatings for orthopedics.

2. Materials and methods

Gradient silver incorporated a-C:H/Ag and silicon incorporated a-C:H/SiOx carbon coatings were synthesized on AISI 316 L medical austenitic steel substrate with use of hybrid Radio Frequency Plasma Assisted Chemical Vapor Deposition/Magnetron Sputtering (RF PACVD/MS) system. Presented technology allows manufacturing thick and well adherent DLC coatings by the application of Ti-Ti_xC_y gradient interlayer synthesized prior the proper coating deposition [9]. Three different silver concentrations were obtained by changing the power density during the magnetron sputtering process between 5 and 10 W/cm^2 for samples marked AgDLC1, AgDLC2 and AgDLC3 (Ag surface concentration 4.5, 8.4 and 15.19 at.%, respectively). A negative self-bias potential of 800 V was used for the synthesis of three series of coatings from CH4/hexamethyldisiloxane gas mixture with flow ratios of 18/3, 16/12 and 14/21 sccm/sccm under pressure of 20 Pa (marked as SiDLC1, SiDLC2 and SiDLC3 with Si surface concentration 0.45, 5.3 and 14.2 at.%, respectively). For comparison bare DLC coatings were also synthetized. Details of the synthesis processes can be found elsewhere [29,30] and the main process parameters are provided in Table 1. Obtained coatings were characterized in terms of morphology, surface topography, mechanical and tribological properties.

Mechanical properties of the coatings were measured using nanoindentation technique on Nano Indenter G200 system (Agilent Technologies). For nanoindentation a diamond Berkovich tip (Micro Star Technologies) and the continuous stiffness measurement mode were used. The tip shape was calibrated by conducting experiments on a fused silica standard and data were analyzed using the Oliver and Pharr [31] approach. Nine experiments were performed on each sample at a strain rate of 0.05 s^{-1}.

Table 1
Main parameters of the coatings' synthesis.

Plasma etching	Pulsed magnetron sputtering of Ti-Ti_xC_y gradient interlayer	Deposition of Ag and Si incorporated DLC
Pressure: 2 Pa Time: 10 min RF bias: -800 V Ar flow: 15 sccm Temperature: <200 °C	Pressure: 0.5 Pa Time: 12 min RF bias: -300 V Power density: 24–30 W/cm^2 Ar flow: 9 sccm CH_4 flow: 1–7 sccm Temperature: <200°C	**AgDLC** Pressure: 20 Pa RF bias: -800 V Precursor: Ar/CH_4 Power density: 5–10 W/cm^2 **SiDLC** Pressure: 20 Pa RF bias: -800 V Precursor: CH_4/HMDSO 18/3–14/21 sccm

The chemical structure of all analyzed coatings and inside the wear tracks after reciprocating sliding tests was investigated by Raman spectroscopy using inVia (Renishaw) spectrometer working with 532 nm wavelength.

Surface structure and morphology were examined using scanning electron microscope JSM-6610LV (JEOL). The phase composition analysis was made by the X-Ray diffraction (XRD) method using an Empyrean diffractometer (Panalytical) working with Co Kα radiation ($\lambda = 0.17903$ nm). The Grazing Incident XRD (GIXRD) mode with an incident beam angle of 0.5° was applied. The average size of silver crystallites was calculated using Debye-Scherrer's formula [32]: $D = K\lambda / B_{hkl} cos\theta$, where D - crystallite size, K - shape factor (for spherical crystals with cubic symmetry equal to 0.94), λ - wavelength of Co K_α radiation, B_{hkl} – full width at half maximum of the peak and θ – Bragg angle. Studies of X-ray photoelectron spectroscopy were carried out using ESCALAB-210 system (VG Scientific) equipped with non-monochromatic Al ($K_\alpha = 1486.6$ eV) X-ray source operated at 14.5 kV and 20 mA. Experimental spectra were deconvoluted using Avantage 4.84 (Thermo Electric) software and the background was fitted using Shirley inelastic background subtraction [33].

Surface morphology, topography and lateral force measurements were performed under ambient conditions using Multimode atomic force microscope equipped with Nanoscope V controller (Bruker Corporation). Topography measurements were made in tapping mode and the size of the images were 1×1 μm. Commercial silicon cantilevers type HQ:NSC15 (MicroMasch) with nominal tip radius ~8 nm, cantilever spring constant of 40 N/m and resonant frequency of 325 kHz were used. Image acquisition was performed with use of Nanoscope 7.3 software and further image processing was done using Nanoscope Analysis 1.5 (Bruker Corporation) and MountainsMap Premium 5.0 (Digital Surf) software. The average roughness (Ra) and root-mean square roughness (RMS) of the samples were defined as average values taken from 512 surface profiles. The size of globular domains of Ag-DLC coatings was calculated using SPIP 6 image processing software (Image Metrology A/S). Prepared topography images were processed using Pore and Particle analysis option in Watershed – Packed Features segmentation mode (this method is used when the image is fully covered by adjoining features of the same type with no spacing in between).

For friction measurements the areas of 100×100 nm were used at increasing loads up to ~50 nN (10 normal loads ramping equally over the single image) at 1 Hz scan rate according to the procedure described already in our previous papers [34,35]. Two different types of AFM tips: commercial silicon cantilevers type HQ:CSC37 (tip radius = 8 nm, spring constant = 0.3 N/m, MicroMasch) and diamond-like carbon (DLC, hydrogen-free ta-C) coated probe cantilevers type HQ:XSC11 (MicroMasch) with resulting tip radius ≤20 nm and nominal cantilever