CORROSION BEHAVIOR OF DLC COATING ALLOYED BY TITANIUM

Luděk JOSKA, Jaroslav FOJT, *Ladislav CVRČEK, **Vítězslav BŘEZINA, ***Jaroslav Málek
Institute of Chemical Technology Prague, Technická 5, 166 28 Prague 6, joskal@vscht.cz
*HVM Plasma, Na Hutmance 2, 158 00 Prague 5
**Masaryk University, Faculty of Medicine, Komenského sq. 2, 602 00 Brno
***UJP Praha, Nad Kamínkou 1345, 156 00 Prague 5

Abstract

Properties of DLC layers provide for their broad use in medical applications. Their tribological properties are frequently utilized in big joint implants. Another benefit is offered by their barrier effect. In the frame of presented work corrosion behavior of DLC-Ti alloyed coatings formed on TiNbTa alloy in environments to which dental implants may be exposed was studied. Electrochemical impedance spectroscopy, XPS and a cell colonization test were employed in the study.

Influence of DLC alloying by titanium was tested on samples with 3 levels of titanium amount. According to results of XPS analysis, surface concentration of titanium was 3.4, 10.2 and 23.6 % at. Unambiguous and marked peak of titanium carbide was detected only in the case of highest concentration of titanium. Corrosion resistance of TiNbTa/Ti/DLC and TiNbTa/Ti/DLC-Ti was in low-aggressive physiological solution slightly different nevertheless very high in both cases. Electrochemical behaviour of carbon was significantly suppressed by titanium; character of EIS spectra was more capacitive than in the case of pure DLC. Decrease of pH did not influence the level of charge transfer resistance (polarization resistance). The main disadvantage of titanium - sensitivity to fluorides - was emphasized by alloying. Colonization by cells was slightly increased on alloyed samples in comparison with unalloyed DLC.

Keywords: DLC layer, titanium, alloying, corrosion properties, EIS, XPS

1. INTRODUCTION

Layers of the DLC (diamond-like carbon) type are used in human medicine in the treatment of implants surfaces [1]. They offer basically two ways of application: their excellent tribological properties are used on friction areas of big joint replacements, and they may also serve as bio-inert barrier layers on implants made of materials likely to cause a negative response of the organism (e.g. alloys containing nickel, TiAlV, etc.). In the latter case they are able to eliminate the corrosion process relating to the release of soluble corrosion products into the body environment. However, one of the current aims in the field of transplantology is to achieve the fastest possible osseointegration, which requires that the implanted surfaces should be bioactive.

β-titanium alloy Ti36Nb6Ta is a material that might be used in the construction of both orthopaedic and dental implants in the future. In the case of joint replacements, the advantage of coating rests in good tribological properties of DLC layers because a direct combination of titanium and its alloys with, e.g., UHMWPE is not suitable for long-term exposure [2-4]. A pure DLC coating is bio-inert, yet for its application it would be desirable to ensure its bioactivation while preserving its tribological properties. DLC alloying with titanium might represent one of the possible solutions [5]. The use of a bioactive barrier DLC layer also seems to be a good choice for dental implants made of materials of the CoCrMo type because part of their surface gets in contact with the soft tissue. It is specific for
stomatology and important from corrosion point of view that the implants may get in contact with medical preparations containing high amounts of fluorides which destabilize titanium [6].

The presented work studied corrosion behavior of DLC coatings alloyed with titanium on experimental titanium alloy Ti36Nb6Ta. Corrosion behavior in a physiological solution with two pH levels and an addition of fluoride ions was evaluated. The surface colonization with cells was also tested within the study.

2. MATERIALS AND METHODS

Flat substrates with a diameter of 14 mm and thickness of 3 mm made of \( \beta \)-titanium alloy Ti36Nb6Ta (UJP Prague) were used for the coating. The surface was treated to 2 levels of roughness: polished specimens (P) with a roughness of \( R_a = 0.08 \) \( \mu \)m modelling the sliding surfaces of implants, and specimens jet-blasted with corundum (JB) with \( R_a = 1.00 \) \( \mu \)m corresponding to one of the possible surface treatments of implants.

Ti-C:H coatings were deposited in Hauzer Flexicoat 1200 equipment (configuration with five planar magnetrons, chamber volume 1000 L). The substrates were first degreased in an alkaline ultrasound bath, and subsequently rinsed in deionized water and dried in vacuum. Prior to their placement in the deposition equipment, the substrates surface was cleaned in argon plasma. The deposition itself started with the preparation of an adhesion inter-layer of pure Ti, followed by a gradient layer with a composition changing from Ti to Ti-C:H. This layer was deposited by way of non-equilibrium magnetron sputtering from Ti targets (99.5 %) in an Ar atmosphere (99.999%), with C\(_2\)H\(_2\) (99.6%) added step by step. After achieving the selected flow of C\(_2\)H\(_2\), deposition of the functional Ti-C:H layer for the selected flows of 60, 100 and 140 sccm C\(_2\)H\(_2\) followed. A bias of -200 V, deposition temperature of 200°C, an achieved limiting pressure of 2.10\(^{-3}\) Pa, and a deposition pressure of 0.8 Pa were applied. The layers thickness was determined using the calotest method, adhesion to the coated substrate was measured by way of the scratch test (CSEM Revetest).

XPS spectra were measured using an EscaProbe P (Omicron) spectrometer with an excitation monochromatic Al K\(_\alpha\) (\( E = 1486.6 \) eV) source. Survey spectra in the binding energies range of 280-550 eV and detailed spectra of Ti 2p, C 1s and O 1s were scanned. Energy was normalized to a gold peak 4f7/2 (binding energy \( E_b = 83.98 \) eV [7]).

Electrochemical impedance measurements were conducted in a standard way (measurement at \( E_{ocp} \), frequency range 100 kHz - 1 mHz, excitation ac signal 20 mV), using potentiostat PCI4/750 with an ECM 8 multiplexer (both Gamry). A silver/silver chloride electrode with a chloride ions concentration of 3 mol/L was used as a reference electrode. An aerated physiological solution (9 g/l NaCl), physiological solution with pH adjusted by way of phthalate buffer to a value of 4.2, and the same solution with 200 ppm fluoride ions added served as exposure environments. The specimens were sterilized (120°C/20 minutes) prior to the exposure. Measurements were conducted in PTFE cells at 37°C for 168 hours, with periodical spectra scanning once in 24 hours. Equivalent circuits shown in Fig. 1 a-c were used for the spectra course analysis. The equivalent circuit a) is a simple circuit
generally used in analyzing corrosion systems with one porous layer, b) is a circuit applied in analyzing corrosion systems with one non-porous layer, and c) describes a corroding/passive system. \( R_{el} \) stands for the electrolyte resistance \([\Omega \text{cm}^2]\). \( R_x[\Omega \text{cm}^2]\)-CPE \(_x\)[Ss/cm²] are RC elements corresponding to the respective phase boundary.

Biological tests were conducted on sterilized specimens. Cell line MG 63 cultivated in a MEM medium with 5% fetal bovine serum added was used for the colonization test. Cells were inoculated directly on the surface of the studied material, and the area colonized by the cells after 72 hours of cultivation was evaluated. After the end of exposure, the cells were fixed and stained using the Giemsa stain diluted 10x with distilled water. The area occupied by the cells on the specimen surface was microscopically evaluated on ten picture fields as minimum, the field of view was \(1.29 \times 10^6\) pixels. An area of identically cultivated cells on an unalloyed DLC layer was used for control.

3. RESULTS AND DISCUSSION

The Ti inter-layer thickness was 0.4-0.5 μm for all coating variants with the structure Ti/gradient Ti-C:H/Ti-C:H. The overall thickness of the Ti-C:H 60 coating was 1.5 μm, of which 0.8 μm accounted for

![XPS spectra of DLC layers alloyed by titanium.](image-url)

Fig. 2 XPS spectra of DLC layers alloyed by titanium.
the upper functional layer. For the Ti-C:H 100 coating, the overall thickness was 1.6 µm including a functional layer of 0.8 µm, and for Ti-C:H 140 it was 1.4 µm including a functional layer of 0.6 µm. The coating adhesion was impaired at a critical load of 30 N in all cases.

Using the XPS method, titanium content in individual specimens was found on the level 3.4 % at. (Ti-C:H 140), 10.2 % at. (Ti-C:H 100), and 23.6 % at. (Ti-C:H 60). In addition to carbon, oxygen and titanium, nitrogen presence was also recorded on the specimens surface. The state of the surface is documented by way of survey and regions C1s and Ti 2p spectra in Fig. 2. At the lowest titanium concentration in the DLC layer, doublet Ti 2p corresponds to a set of oxides TiO, Ti2O3 and TiO2, with concentration increasing in this order. The carbon peak (C 1s) is not in this case deformed in any significant way. An increasing Ti concentration in the layer brings about a change both in titanium Ti 2p and C 1s spectra. In the case of Ti 2p, the signal grows disproportionately at an energy of 455 eV, where the contributions of TiO (455.2 eV) and TiC (454.9 eV), and possibly also sub-stoichiometric carbides overlap [7]. TiC existence in the layer can be clearly detected in the C 1s spectrum, where a signal appears on the binding energy 281.6 eV, corresponding to the carbon bond in TiC [7, 8].

In terms of the surface state, specimens with the lowest level of alloying were the “purest”. Nevertheless, based on the assumed applications, specimens alloyed with 10.2 % at. of titanium (Ti-C:H 100) were chosen for further study. The decision was also affected by the technological point of view. Stability of the process of forming a layer with the lowest level of alloying is rather problematic, which might also cause problems in the reproducibility of layers preparation.

![Graphs](image)

**Fig. 3 EIS spectra of Ti36Nb6Ta with unalloyed DLC layer.**

Fig. 3 shows electrochemical impedance spectra of Ti36Nb6Ta specimens with unalloyed DLC coating deposited on both evaluated surfaces (P and JB), exposed at both pH levels of the physiological solution. The course of all dependences – spectra measured at the 24th and 168th hour – makes it clear that the behavior of coated systems was stable, with spectra practically unchanged throughout the exposure. Impedance dependences of specimens with a polished surface correspond to a system with two time constants. This behavior is an expectable response of the layered structure. The spectra were analyzed using two types of equivalent circuits as shown in Figs 1 a) (porous layer) and 1 b) (non-porous layer). Success of the analysis was on a comparable level in both cases. The selected models of the phase boundary were able to describe the behavior of systems with minimum deviations of calculated values from experimental data. The course of the spectra clearly indicates systems with a very low rate of electrochemical reactions. In the ideal case – in view of graphite inertness - these should be only reactions of the environment components. The basically identical result of analysis conducted using both selected equivalent circuits indicates that this type of EIS measurement does not allow for a clear decision on the layers porosity.

The situation of specimens with a jet-blasted surface was different. In this case the spectra reflect the layered character of the structure (the course of the phase clearly changes at frequencies below 1 Hz),
with the coatings porosity clearly manifesting itself in this case. The quality of experimental data fitting by way of an equivalent circuit as shown in Fig. 1 a) was higher and the errors of parameters estimates were lower as compared with the application of the model shown in Fig. 1 b).

Alloying of a DLC layer with titanium led to a change in the impedance response, mainly in the case of layers deposited on the polished surface. The spectra were formally identical with dependences measured on jet-blasted specimens with an unalloyed DLC layer. Titanium presence in the DLC layer led to prevailing interaction of titanium with the environment on the DLC-electrolyte phase boundary. In terms of medical applications, this fact is positive as it indicates the possibility of affecting the bioactivity of the layer-body environment phase boundary. Unalloyed DLC coatings are bio-inert while titanium oxides may be

(bio)activated by way of chemical-thermal treatment. The spectra reflect the layered character of the specimens, with a clear change in their course at frequencies below 1Hz. The EIS spectra analysis of specimens with a polished surface led to the same result as that recorded for unalloyed layers – success of experimental data fitting with functions generated on the basis of both equivalent circuits was comparable. In contrast, the effect of porosity was unambiguous in the case of jet-blasted surfaces. DLC layers deposited on a jet-blasted surface displayed porosity regardless of the alloying. Consequently, they cannot be applied as barrier layers.

Addition of fluoride ions to the physiological solution with pH=4.2 resulted in a dramatic change in the course of the spectra. A drop in impedance confirmed instability of titanium oxides in an environment containing fluorides/hydrofluoric acid [6], which also applied in the case of titanium bound in a DLC layer. Quite surprisingly, spectra may be in all cases (both P and JB) successfully fitted only by way of an equivalent circuit modeling a non-porous layered system. This may be due to the layer pores being closed with corrosion products [9]. Based on these results and given the common use of fluorides in medicinal preparations, the application of Ti-alloyed layers in stomatology is likely to be rather limited.

Fig. 4 EIS spectra of Ti36Nb6Ta coated by DLC layer alloyed by titanium (physiological solution, 37°C).

Fig. 5 EIS spectra of TiNbTa with a DLC layer alloyed with titanium (surface state P, physiological solution pH=4.2/200 ppm F, 37°C).

Fig. 6 EIS spectra of TiNbTa with a DLC layer alloyed with titanium (surface state JB, physiological solution pH=4.2/200 ppm F, 37°C).
Fig. 7 shows the results of the colonization test. The alloyed specimens were not treated in any way in order to increase their bioactivity prior to the biological testing. The colonization test showed a slight increase in the occupation of the alloyed DLC layer surfaces with cells as compared with unalloyed layers. However, the difference of values was not statistically significant. At the same time, higher colonization was noted on specimens whose surface was jet-blasted prior to the coating in comparison with polished surfaces, yet no statistically significant difference was proved in this case either. These results give hope that subsequent treatment may lead to a more distinct growth of colonization on the alloyed specimens surface.

4. CONCLUSIONS

DLC coatings alloyed with titanium at a level of 3.4 % at. to 23.6 % at. were deposited on a titanium β-alloy Ti36Nb6Ta within the study. At the highest titanium concentration, its significant amount was bound in TiC carbide. Corrosion behavior of specimens with an alloyed layer was significantly different from pure DLC coatings. Electrochemical reactions of the environment on graphite surface were overlapped by titanium interaction with the electrolyte. This fact is rather promising as far as application on implants is concerned as it indicates the possibility of modifying the bioactivity of titanium oxides by way of subsequent treatment. Alloying with titanium led to a slight increase in the surface colonization with cells.

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REFERENCES