MECHANICAL PROPERTIES OF a-C:H/Ti LAYERS ON PROSTHODONTIC CoCr AND NiCr ALLOYS

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Abstract

Co-Cr and Ni-Cr alloys are widely used in dental implants production. However, there is a risk connected with application of this kind of materials like allergy and methalosis caused by Cr. Ni ions, very dangerous for patients’ health and life. Moreover metal ions released into human body can affect inflammation of the surrounding tissue. Biomaterials’ surface treatment by the deposition of diamond-like carbon films can noticeably improve the corrosion and mechanical features. Widely discussed in world’s literature problems with adhesion of DLC layers can be solved by the deposition of gradient a-C:H/Ti layer. Due to that, it is possible to manufacture thick and well adherent carbon layer on the implant’s surface which will constitute a very good protection against wear and corrosion. Our goal was to evaluate the mechanical properties of a-C:H/Ti layers deposited on CoCr and NiCr alloys in hybrid deposition system RF PACVD/MS and to find the influence of layer thickness on the selected properties. As the result of the investigation it was noticed that deposition of a-C:H/Ti layer improves the mechanical properties of CoCr and NiCr alloys. High hardness and good adhesion of gradient carbon layers makes them a very perspective material for this kind of applications.

Keywords: carbon layer, corrosion, wear resistance, dental implant, gradient, methalosis

[Engineering of Biomaterials, 85 (2009), 2-5]

Introduction

Metals and their alloys are commonly applied in dentistry. They are used both in prosthodontics and in orthodontics. All the elements of orthodontic braces, such as brackets, archwires, bands, springs, are made of metals. Elements of fixed and removable dentures (cast metal partial dentures, acrylic partial and full denture claspers, splints, bridges, crowns, endodontic posts, etc.) are made of these alloys. Such a common application of metals and their alloys results from the lack of any alternative material that would have better or comparable properties (especially resistance and durability). Metals possess appropriate stiffness, elasticity and can be easily formed by means of different methods.

Corrosion is the main reason of deterioration of essential properties in a metal or non-metal material. These phenomena occur due to the presence of high amount of chloride ions, proteins and enzymes, pellicule and acidic bacteria metabolites. Moreover the final effect of the metal corrosion processes are metal ions released during corrosion process that penetrate into the surrounding tissues, as well as galvanic currents. All factors contribute to the fact that no available basic metal alloy can resist biological corrosion. Cobalt chromium alloys do not exhibit sufficient corrosion resistance in the oral cavity [1]. However, they are still applied in dentistry because of a reasonable price alternative for expensive noble metal alloys. In order to improve their corrosion resistance, they are subjected to a variety of surface modifications that enhance biological tolerance and corrosion resistance of these alloys. Among many different modification methods including synthesis of thin films on the surface, carbon layers deposition is one of the most promising methods of medical implants protection against corrosion [2,3]. Carbon, as an element, possesses an outstanding corrosion resistance and good biocompatibility. These properties depend mostly on the respective amount for an allotropic form of carbon, diamond or graphite structure. Modification of metal elements surfaces with carbon layers should guarantee their enhanced corrosion and mechanical properties [4,5].

Materials and methods

Co-Cr and Ni-Cr alloys cast cylindrical samples, 15 mm in diameter and 10 mm in height, were used. Specimens were subjected to grinding followed by polishing with use of 3 μm diamond suspension. The chemical composition of the alloys is presented in TABLE 1 and 2.

**TABLE 1. Chemical composition of NiCr alloy.**

<table>
<thead>
<tr>
<th>Contents of the elements – mass [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
</tr>
<tr>
<td>23.89</td>
</tr>
</tbody>
</table>

**TABLE 2. Chemical composition of CoCr alloy.**

<table>
<thead>
<tr>
<th>Contents of the elements – mass [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
</tr>
<tr>
<td>29.63</td>
</tr>
</tbody>
</table>

For a-C:H/Ti layers synthesis in presented investigation a new RF PACVD/MS deposition system was used. The idea of this technology is the connection of radio frequency plasma assisted chemical vapour deposition method with magnetron sputtering system in one reaction chamber. In this method 200 nm thick gradient Ti-C interlayer is employed to improve the adhesion and to minimise the internal stress of thick carbon layer deposited subsequently on the top. More precise description of presented technology can be found in works [6,7]. Very good corrosion properties obtained for REX 734 steel covered with a-C:H/Ti layers [8], seems to be a very attractive solution for this kind of application. Before the deposition process, samples were ultrasonically cleaned in acetone. Reaction chamber was pumped away to a pressure of 2×10⁻³ Pa. Deposition process was preceded by 10 min etching in Ar plasma with self bias -720 V. Flow of reaction gases during the deposition process were in the range of 9-12% for argon and 0-30% for methane. Carbon layer on the top was deposited with self bias -600 V. Thicknesses of a-C:H/Ti gradient layers were 0.7 and 1.2 μm.
The aim of this work was to investigate the mechanical properties of a-C:H/Ti layers deposited onto Co-Cr and Ni-Cr alloys and to find the influence of coating thickness on these parameters.

Surface morphology examinations were conducted with the use of HITACHI S-3000N scanning electron microscope. Qualitative analysis was performed using X-Ray microanalysis with energy dispersion (EDS) spectrometer. Veeco MultiMode V Scanning Probe atomic force microscope was used to investigate the surface topography and roughness parameters.

Hardness was determined using standard Berkovich diamond tip with a semi angle of 65.35 degrees and rounding radius ≤20 nm. The investigation was performed using MTS NANO INSTRUMENTS G-200 nanoindenter. The measurement was performed with the Continuous Stiffness Measurement (CSM) option [9] which allows for continuous contact stiffness measurement during the penetration process not just at the point of unloading (maximum load) which noticeably improves the investigation procedure. CSM method is ideal for measuring thin layers, where properties change according to the thickness of the coating. The advantage of this method is continuous information concerning hardness and elastic modulus obtained as a continuous function of depth for a single indentation experiment [9-11]. Nine 2000 nm deep measurements were taken for every sample and the results were averaged. Adhesion examinations were carried out by the scratch test method using a diamond cone penetrator. Investigation of fracture and delamination of the layer was based on friction coefficient changes during the scratch process and optical microscopy observations [9,11]. Rounding radius of the tip was 0.98 μm with an angle of 87.7 degrees. The examinations were performed using gradually increasing penetrator load of 0 to 160 mN, with a speed of 10 μm/s, on a distance up to 800 μm. Five scratch measurements were taken for every sample and the results were averaged.

Results and Discussions

SEM investigations of the layers surface topography (FIG. 1) shows that it is smooth without any delaminated places. Moreover there are no cracks in the layer’s structure. It is especially important in the case of carbon layers where the thickness is limited by the high internal stress of the coating. Cracking and delamination of the layer occurred when the optimal thickness passes the limit are the main reason of corrosion processes. Lack of fractures, scratches, pits, etc. ensures adequate protective properties of the coatings deposited on prosthodontic elements and thereby provides anti-corrosion properties. On the basis of SEM investigations it can be stated that thick carbon layer will limit the corrosion products release into the oral cavity as well as the metal ions transfer.

Chemical composition of the layers investigated with the use of EDS analysis with 25 kV acceleration voltage (FIG. 2) proves that only carbon is present in investigated films without any other impurities. Peaks from other elements like Mo, Co, Cr and Ni come from the substrate. Ti peaks which appear in the EDS spectra are from the gradient Ti-C interlayer which improves the adhesion. Authors of the work didn’t examine the phase composition of deposited layers but on the basis of earlier works with the use of the same carbon layers deposition technology [12], it can be stated that investigated coatings are amorphous hydrogenated carbon layers DLC.

Wear resistance of the protective coatings strongly depends on the hardness. Generally with increasing hardness the greater wear resistance is obtained. However, usually high hardness is the main reason of fragility of the layer, especially in the case of the carbon coatings. In presented studies hardness of investigated a-C:H/Ti layers was in the range of 20.2-21.9 GPa (FIG. 3).
No significant differences between the hardness of the layers on both substrates were observed. Lower hardness values registered for 0.7 μm thick gradient layers are due to higher influence of the substrate which hardness is much lower than one of the coating (3.2 GPa for NiCr alloy, 4.5 GPa for CoCr alloy) (FIG. 4). Such high hardness of the protective coating should ensure sufficient protection against wear occurred in the oral cavity. Gradient of chemical composition reduces the internal stress of the layer thus even thick and hard a-C:H/Ti coating should be resistant against brittle cracking. But this problem needs further investigations.

During the adhesion measurements authors decided to determine the critical force on the basis of the optical microscope observations of the layer’s surface after the adhesion test. This is because during the measurement process before the total break off of the continuity between the layer and the substrate much earlier the characteristic cracks appear on the surface (FIG. 5,6). Every single crack or chip in the layer’s structure uncovers the substrate material which causes the lost of anti-corrosion properties with all the consequences. Critical forces determined for investigated alloys are presented in FIG. 7. As it was mentioned above the critical force is much lower than it appears from the friction coefficient vs load applied graph (FIG. 8).
THE INFLUENCE OF OXYGEN PLASMA ON SURFACE FUNCTIONALITIES OF CELLULOSE FIBRES

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Abstract

Quality and quantity of groups in cellulose fiber is possible to change by chemical procedure (for example by using strong oxidizing agent). One of other possible methods to change the chemical groups in cellulose fibers is plasma treatment. In this study for plasma treatment a source of Diffuse Coplanar Surface Barrier Discharge (DCSBD) was used. Air plasma treatment of cotton at atmospheric pressure was made in a wide time scale. The chemical changes of cotton were observed and discussed.

Keywords: cotton, plasma treatment, DCSBD

[Engineering of Biomaterials, 85 (2009), 5-7]

Introduction

Cellulose fibers are known by their complicated chemical structure, that is not possible describe by one chemical formula. In cellulose fibers not only hydroxyl groups, but also other chemical groups in smaller concentration, e.g. carbonyl or carboxyl group are present. Oxidated groups increase the sorption of dyes and other chemicals into the fibers. High degree of oxidation is typical for some special cellulose derivatives, for example oxyccellulose, which has many applications in technical and medical branches.

The oxidized cellulose (oxycellulose) is used in many medical and related areas such as: absorptive material to stop bleeding, bodying agent in pharmaceutical preparations, coating material in the formulation of encapsulated hemostatic agents.

Plasma is a medium of energy transport. Molecules in plasma are of high energy level and high degree of ionization. Plasma is a source of energy and a source of radicals, which are able to estimate chemical groups in a thin layer of fiber surface. By the help of sorption (dyeing) test quantity of carboxyl groups in the fiber was determined. Probability of reaction with these non-hydroxyl groups is lower than 1% of hydroxyl groups quantity. By the oxidation of hydroxyl groups the content of carbonyl and carboxylic groups is lower than 1% of hydroxyl groups quantity. Probability of reaction with these non-hydroxyl groups is smaller than 1:100. By the oxidation of hydroxyl groups is smaller than 1:100.

Cellulose fibers were documented by the use of instrumental analytical methods FTIR and XPS, which are able to estimate chemical groups in a thin layer of fiber surface. By the help of sorption (dyeing) test quantity of carboxyl group in the fiber was determined. Quantity of carboxyl groups was estimated with the use of so-called “copper number”. Possible changes of fiber surface morphology (roughness) were monitored with the use of scanning electron microscopy.