Corrosion resistance of various bio-films deposited on austenitic cast steel casted by lost-wax process and in gypsum mould

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Abstract

This work is the next of a series concerning the improvement of austenitic cast steel utility predicted for use in implantology for complicated long term implants casted by lost-wax process and in gypsum mould. Austenitic cast steel possess chemical composition of AISI 316L medical steel used for implants. In further part of present work investigated cast steel indicated as AISI 316L medical steel. Below a results of electrochemical corrosion resistance of carbon layer and bi-layer of carbon/HAp deposited on AISI 316L researches are presented. Coatings were manufactured by RF PACVD and PLD methods respectively.

Obtained results, unequivocally indicates on the improvement of this type of corrosion resistance by substrate material with as deposited carbon layer. While bi-layer of carbon/HAp are characterized by very low corrosion resistance.

Keywords: Carbon coatings, Hydroxyapatite, Corrosion, Austenitic cast steel

1. Introduction

Designing of metallic implants is a huge problem for engineers nowadays. Materials destined for short-term implants (ex.: orthopedics stabilizers) should possess high biotolerance, high corrosion resistance and strength properties and simultaneously do not creates durable chemical bond with a host bone tissue after implantation. Required high mechanics of materials and implants operational reliability and on the other side no application of toxic (allergenic) elements in biomaterials causes kind of materials use restrictions to austenitic steel, cobalt matrix alloys and titanium alloys. In spite of tests it was not able to eliminate an elements harmful for human organism as: chromium, nickel and vanadium. An attempt of limit of adverse elements influence to the human body are surface modifications of implants predicted for short-term ones by protective coatings deposition.

Very satisfying results obtained by carbon layers deposition [1-5]. Those carbon films, widely applied in medicine, are valuable in terms of their biological, mechanical anticorrosive properties. Such layers are characterized by high biocompatibility and an ideal bioinertness results from lack of immunological respond of living organism to the implant with as-deposited carbon film. Moreover, corrosion resistance of implant is increased and excellent barrier against metal ions is created.

The extremely high requirements relates to those for long term. These implants should work properly in tissue environment for at least 20 years (ex.: hip endoprothesis, backbone stabilizers etc.). They should be dielectrics, possess high strength, corrosion resistance, biotolerance with human body, creates durable bonding with bone tissue. Fulfil of all mentioned requirements by
implant made of one kind of material is impossible. Above features are able to obtain by deposition on metallic implant surface the hydroxyapatite layer which has attracted widespread interest because of its biocompatibility and bioactivity resulting from its chemical and crystallographic similarities to those of the human bone. As it is mentioned above one of the most important feature of implants is its corrosion resistance. The present study is focused on investigation of protective properties of carbon/HAp composite coatings in comparison with single carbon or HAp coatings deposited on AISI 316L medical steel. These protective properties were evaluated as a results of corrosion parameters obtained in Tyrode’s solution.

Austenitic cast steel possess chemical composition of AISI 316L medical steel used for implants (16.48%Cr, 13.38%Ni, 2.49%Mo, 0.022%C, 0.583%Si, 1.669%Mn, 0.021%P, 0.022%S). In further part of present work investigated cast steel indicated as AISI 316L medical steel.

2. Research methodology

Material used for investigations was AISI 316L medical steel (ISO 4967-1976EO) after solution heat treatment. Samples with 8mm diameter and 5mm of thickness were prepared. Before layer deposition they were undergone of grinding (till 1200µm abrasive paper) and polishing with use of diamond paste. Carbon film with thickness of about 120nm was deposited by RF PACVD method [11]. Corrosion resistance of AISI 316L with and without carbon film was measured in Tyrode’s physiological solution. Its chemical composition is shown in table 1.

Table 1.
Chemical composition of Tyrode’s solutions

<table>
<thead>
<tr>
<th>Component concentration [g/dm³] of distilled water</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>8,00</td>
</tr>
<tr>
<td>CaCl</td>
<td>0,20</td>
</tr>
<tr>
<td>KCl</td>
<td>0,20</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>1,00</td>
</tr>
<tr>
<td>NaH₂PO₄</td>
<td>0,50</td>
</tr>
<tr>
<td>MgCl₂·6H₂O</td>
<td>0,10</td>
</tr>
<tr>
<td></td>
<td>6,9</td>
</tr>
</tbody>
</table>

Measurements were carried out with use of ATLAS – SOLLICH corrosion tester equipment. Temperature of Tyrode’s physiological solution was 37°C in a Glass electrolytic cell. This cell had a sample as working electrode E_w, Pt foil as counter electrode E_c and calomel electrode in saturated NaCl solution as the reference electrode E_ref (all potentials in this work are given versus this calomel electrode, E° = 0,236 Vvs. SHE). Exposed area of each sample was ca. 0.35 cm². All measurements were done using PGSTAT 30 Autolab EcoChemic potentiostat/galvanostat. Typical measurement cycle was consisted of: (i) the gathering of open circuit potentials (OCP) for determination of corrosion potential E_cor; (ii) registration of potentiodynamic characteristics according to Stern-Geary method (potential range from -0.20mV to +0.20mV round corrosion potential E_cor and potential scan rate v = 0.5 mV•s⁻¹) for determination of polarization resistance R_p which was calculated using CorrView (Scribner Associates Inc.) software; (iii) registration of potentiodynamic characteristics in a wide anodic polarization range (from ca. E_cor − 0.1V to potential AT chich current density achieved ca. 5 mA•cm² – at this potential the polarization direction was reversed, v = 1 mV•s⁻¹) for determination a type of corrosion and its main parameters. Results of this investigations are presented in figures 1÷3 and in table 2.

3. Results

Table 2.
Change of corrosion potential (E_k), polarization resistance (R_p) and current corrosion I_o for AISI 316L without carbon layer and with carbon layer

<table>
<thead>
<tr>
<th>Sample</th>
<th>E_k [mV]</th>
<th>R_p [Ω/cm²]</th>
<th>I_o [A/cm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>AISI 316L</td>
<td>- 0,12</td>
<td>2,36 E + 0,6</td>
<td>1,10 E - 0,8</td>
</tr>
<tr>
<td>AISI 316L + carbon layer</td>
<td>- 0,006</td>
<td>3,95 E + 0,6</td>
<td>6,63 E - 0,9</td>
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![Image of graph showing change of corrosion potential (E_k), polarization resistance (R_p) and current corrosion I_o for AISI 316L without carbon layer and with carbon layer.](image-url)
From fig. 1 and table 2 analysis results that corrosion potential $E_{\text{cor}}$ for sample of AISI 316L steel coated with carbon is more positive in comparison with uncoated steel. Value of corrosion potential increases in positive way (fig.1a), increases also polarization resistance (fig.1b) as result the corrosion current decrease (fig.1c).

From the investigated potentiostatic curves (fig.2) results that manufacturing of carbon film on AISI 316L as a substrate causes significant decrease of currents in anodic range and maintain of wide passivation scale with simultaneous displacement of corrosion potential to the positive way in relation to the steel without coating. Potential from which intensive corrosion digestion begins of passive layer is clearly shifted into anodic direction for samples with carbon films in comparison with pure samples.

Potentiodynamic characteristics (fig.3), which enable to assess of pitting corrosion resistance indicated that AISI 316L steel coated by carbon layer is much more resistant on this type of corrosion (limits releasing of corrosion products to human organism) what is one of the main requirement destined on implants.

Scanning microscope observations carried out after corrosion measurements confirmed that in case of AISI 316L steel without carbon layer crevice-pitting corrosion proceed while for AISI 316L with carbon layer no pitting corrosion was observed but typical symptom was in this case crevice corrosion (fig.4).
Corrosion resistance of AISI 316L coated by hydroxyapatite layer, with an average thickness of 500nm obtained by PLD method [11] and bi-layer of carbon/HAp measured in the same conditions and parameters as medical steel with and without carbon films.

As results from table 3 and figure 5 manufactured on AISI 316L by PLD method HAp layer reveal corrosion resistance close to the pure AISI 316L steel but higher than sample with bi-layer of carbon/HAp. In the last case value of corrosion potential is the highest in negative direction (fig.5).

From the investigated potentiodynamic characteristics (fig.6) results that the weakest pitting corrosion resistance possess bi-layer of carbon + HAp. This surprising effect results from the fact that during hydroxyapatite manufacturing process by PLD method laser beam defect previous deposited carbon film and in consequence formation of corrosion microcells and growth of pitting corrosion proceed. It was confirmed by scanning microscope investigations (fig. b and c).

On the whole of sample surface coated by carbon/HAp bi-layer corrosion pits were formed what disqualify this kind of coatings for medical applications.

In case of HAp manufacturing by PLD method directly on AISI 316L substrate we can observe only crevice corrosion (fig.7a).

Table 3.
Change of corrosion potential ($E_k$), polarization resistance ($R_p$) and current corrosion $I_o$ for AISI 316L without carbon layer, with carbon layer, with HAp and with carbon layer+HAp. HAp deposited by PLD method

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_k$[mV]</th>
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<tr>
<td>AISI 316L + carbon layer</td>
<td>-0.006</td>
<td>3.95 E + 0.6</td>
<td>6.63 E - 0.9</td>
</tr>
<tr>
<td>AISI 316L + HAp</td>
<td>-0.130</td>
<td>0.89 E + 0.6</td>
<td>2.91 E - 0.8</td>
</tr>
<tr>
<td>AISI 316L + carbon layer+HAp</td>
<td>-0.155</td>
<td>1.74 E + 0.6</td>
<td>1.51 E - 0.8</td>
</tr>
</tbody>
</table>

Fig.4. Surface of AISI 316L (a) and AISI 316L+carbon layer (b) after corrosion studies in Tyrode’s solution. Scanning microscope
Fig. 5. Changes of corrosion potential (a), polarization resistance (b) and current corrosion in potential $E_{\text{kor}}$ (c) for AISI 316L without carbon layer, with carbon layer, with HAp and carbon layer+HAp in Tyrode’s solutions. HAp deposited by PLD method.

Fig. 6. Anodic polarization curves for investigated samples in logarithmic scale of current density, measured in Tyrode’s solution at 37°C for AISI 316L without carbon layer (p1), with carbon layer (p2), with HAp (p3) and carbon layer+HAp (p4). HAp deposited by PLD method.
Conclusions

From the presented investigations results the following conclusions:

- deposited carbon layer on AISI 316L medical steel in significant way improves its electrochemical corrosion resistance what is one of the basic requirements for materials predicts on implants.

- in case of carbon/HAp bi-layer where HAp was deposited by PLD method it is observed very low pitting corrosion resistance what disqualify those layers for practical use.

References


