INVESTIGATION ABOUT THE ABILITY TO BUILD PHOSPHATES ON CoCrMo

Sabina GRIGORESCU¹, Daniela IONIȚĂ², Ioana DEMETRESCU³

The paper aims to built phosphate on CoCr alloy implant surface in order to provide a surface on which bone tissue can grow, forming chemical bonds at the bone/implant interface. The procedure is immersion in simulated body solution (SBF) for 5 and 14 days and is completed with surface and electrochemical characterization. For longer immersion time, the hydrophilic character and surface roughness are increasing. Regarding the electrochemical stability a decrease of corrosion rate was established for the sample immersed for 14 days in SBF solution.

Keywords: phosphate coating, CoCrMo, EIS, cyclic voltammetry, surface analysis

1. Introduction

Cobalt based alloys belong to the group of metals designed for the manufacturing of prosthetic devices [1–4]. Their use is based on the well-established high resistance to corrosion in physiological solution and to their excellent mechanical properties including high tensile and fatigue strength. The reported biocompatibility of cobalt based alloys is linked to the spontaneous formation of a thin (1–4 nm) passive oxide film on their surface [1]. The composition of this layer is predominantly Cr₂O₃ oxide with some minor contribution of other oxides (Co- and Mo- oxides, especially if the film is air formed) [5,6]. The physico-chemical properties of the passive film control the material’s corrosion behaviour, the interaction with tissues and the surrounding part replaced into the body and thus the degree of the material’s biocompatibility. Biocorrosion has been considered one problem for the long durability of implants into human bodies and release of metal ions can cause adverse physiological effects, toxicity, carcinogenicity and metal allergy [7–12]. Co-based alloys, such as CoCr and CoCrMo have been widely used as orthopedic materials for total

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joint, total nee and total hip replacement. However, as a biotolerant material, CoCrMo had some difficulties in connecting directly with the hard tissue[13]. In order to improve the connectivity between implant and hard tissues, the metallic implants were coated with a layer of bioactive calcium phosphate (CaP), consisting mainly of hydroxyapatite(HA)[14-16]. A phosphate coating, as the one presented in this paper, can also act as a barrier between body fluids and the metallic implant and also provides a surface on which bone can grow, forming chemical bonds at the bone/implant interface thus increasing osteointegration. The novel part of the present study is related to the investigation of electrode micel stability in biofluids of the phosphate coating.

2. Experimental part

2.1 Specimen preparation

CoCrMo samples were polished on SiC paper with different grits, in the following order: 320, 600, 800 and 1200 until a mirror surface was obtained. Then, the samples were cleaned under ultrasonication in acetone and ethanol for 15 min each, rinsed with deionized water and dried.

2.2 Chemical and heat treatment

According to the given treatment in literature [17] the samples were immersed in 20 ml of NaOH solution and put them to dry at 160°C for 3 hours. Then the plates were washed with deionized water and left over night in a dark and dry place. The first step of the heat treatment was made at 300°C for 3 hours in air. Then, the CoCrMo samples were introduced in 20 ml of 0.01M HCl solution and kept for 3 hours at 90°C. The second step of the heat treatment was performed at 450°C for 3 hours in air.

After these, the plates were immersed in 96 ml of SBF solution at 36.5°C for 5 days, respectively 14 days. The resulted samples are named S5d for CoCrMo sample immersed for 5 days in SBF solution and S14d for CoCrMo sample immersed for 14 days in SBF solution.

2.3 Surface analysis of the CoCrMo samples after immersion in SBF solution

Surface analysis was done by atomic force microscopy (AFM), contact angle measurements and Fourier Transform Infrared Spectroscopy (FTIR). All measurements were performed after the immersion in SBF solution. The SBF was
prepared according to the method proposed by Kokubo [17] and buffered at pH 7.25. The ion concentration of the SBF is shown in Table 1.

<table>
<thead>
<tr>
<th>Ionic concentration</th>
<th>Concentration (mmol/dm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>142.0</td>
</tr>
<tr>
<td>K⁺</td>
<td>5.0</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>1.5</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>2.5</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>147.8</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>4.2</td>
</tr>
<tr>
<td>HPO₄²⁻</td>
<td>1.0</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>0.5</td>
</tr>
</tbody>
</table>

2.3.1 AFM measurements
Surface roughness of the samples was evaluated with atomic force microscopy (AFM). Contact mode AFM images were obtained using an atomic force microscope from APE Research, Italia. Data acquisition and image processing were performed with Gwydion software.

2.3.2 Contact angle measurements
In order to characterize the wettability of the surface, the contact angle is performed. It was used a Contact Angle Meter –KSV Instruments CAM 100 to evaluate the hydrophilic/hydrophobic balance. By definition, contact angle values between 0 and 90° indicate a hydrophilic surface, and values higher than 90° indicate a hydrophobic character. Each contact angle value is the average of minimum 10 measurements.

2.3.3 FTIR analysis
Using a Spectrum 100 Series FT-IR Spectrometer from PerkinElmer USA, the chemical composition of the coatings was analyzed with Fourier Transform Infrared Spectroscopy (FTIR).

2.4 Electrochemical characterization
In order to characterize the electrochemical behaviour of the samples after they were immersed in SBF solution, Electrochemical impedance spectroscopy (EIS), Tafel and cyclic voltammetry were performed. It was used an Ag/AgCl electrode as reference electrode in all measurements. The electrochemical experiments were done in HANK solutions with the following composition (g/L): NaCl - 8; KCl – 0.4; NaHCO₃ – 0.35; NaH₂PO₄·H₂O – 0.25; Na₂HPO₄·2H₂O – 0.06; CaCl₂·2H₂O – 0.19; MgCl₂ – 0.19; MgSO₄·7H₂O – 0.06; glucose- 1.

2.4.1 Electrochemical impedance spectroscopy measurements
Electrochemical impedance spectroscopy measurements were carried out at room temperature using an Autolab PGSTAT 302 N with NOVA1.7 specific software. The impedance spectra were acquired in the frequency range of 10⁻² – 10⁵ Hz and the applied amplitude of the AC potential was 10 mV.
The EIS cell was formed from a reference Ag/AgCl electrode, a platinum counter electrode, a working electrode and a cylindrical chamber. CoCrMo samples were used as working electrode.

2.4.2 Tafel plots
In order to evaluate the the corrosion potential ($E_{cor}$), current density ($i_{cor}$), passivation current ($i_{pas}$) and corrosion rate ($v_{cor}$) linear polarization measurements were carried out.

2.4.3 Cyclic voltammetry
Using a VoltaLab 40 (PGZ301 Universal Potentiostat & VoltaMaster 4) cyclic voltammetry measurements were performed within the potential domain from -0.8V to +1.5V with a scan rate of 2mV/s.

3. Results and discussion

3.1. FTIR measurements

Fig. 1 shows the FTIR spectrum of the CoCrMo sample after it was immersed in SBF solution for 5 days and which exhibits typical bands characteristics of the hydroxyapatite. It can be seen that bands corresponding to the absorption peaks of OH groups appeared at 3270.88 cm$^{-1}$. The vibrational band of 1029.21 cm$^{-1}$ is mainly attributed to PO$_4^{3-}$ absorption peaks. At 1638.48 cm$^{-1}$ can be seen the peak corresponding to Co$_3^{2+}$ group. The absorption peaks in the sample due to PO$_4^{3-}$ and OH$^-$ show strong intensities in the spectrum. These peaks are the signature peaks of hydroxyapatite (HA).

![FTIR spectrum of S5d](image)

Fig. 1. FTIR spectrum of S5d
3.2 Surface morphology of CoCrMo alloy samples

2D and 3D AFM images of CoCrMo alloy samples after they were immersed in SBF solution for 5 and 14 days respectively, are shown in Fig. 2. The values of average roughness ($R_a$) were computed with Gwyddion software and, with the corresponding contact angle values for these samples, are listed in Table 2.

![AFM images for S5d and S14d](image)

**Table 2**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_a (\mu m)$</th>
<th>Contact angle(°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S5d</td>
<td>0.120</td>
<td>77.46</td>
</tr>
<tr>
<td>S14d</td>
<td>0.179</td>
<td>56.69</td>
</tr>
</tbody>
</table>

For the CoCrMo sample that was immersed for 14 days in SBF the roughness($R_a$) presents an increase and the contact angle values present a decrease. It can be said that the sample immersed for 14 days is more hydrophilic than the one immersed for 5 days.

3.3. Electrochemical characterization of the CoCrMo samples

The electrochemical behavior of the samples was characterized by Tafel, EIS and cyclic voltammetry.
Tafel plots obtained for CoCrMo samples immersed in SBF solution for 5 days, respectively 14 days are presented in Fig.3. Table 3 presents the corresponding corrosion data: corrosion potential ($E_{\text{corr}}$), corrosion current ($i_{\text{corr}}$) and rate of corrosion ($v_{\text{corr}}$). From these data it can be said that CoCrMo sample that was immersed for 14 days in SBF solution has the most electropositive value for $E_{\text{corr}}$, thus indicating the presence on its surface of a more stable structure in what corrosion concerns. The corrosion rate decreases due to the presence of the hydroxyapatitic layer on the surface thus the CoCrMo sample that was immersed for 14 days in SBF solution is more stable than the CoCrMo sample that was immersed for 5 days in SBF solution.

**Table 3**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_{\text{corr}}$ (V)</th>
<th>$i_{\text{corr}}$ (A/cm$^2$)</th>
<th>$v_{\text{corr}}$ (mm/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S5d</td>
<td>-0.34617</td>
<td>$4.77 \times 10^{-6}$</td>
<td>$0.440 \times 10^{-4}$</td>
</tr>
<tr>
<td>S14d</td>
<td>-0.02208</td>
<td>$2.23 \times 10^{-6}$</td>
<td>$0.203 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

The Autolab NOVA software was used to evaluate the electrochemical impedance spectroscopy analysis and the corresponding Nyquist plots of the impedance data. In Fig.4 Nyquist plots are presented while the corresponding equivalent electric circuit data are listed in Table 4. For CoCrMo sample immersed for 5 days in SBF solution a single constant circuit was proposed while for CoCrMo sample immersed for 14 days in SBF solution a two time constants circuit was proposed, as shown in Fig.5.
Fig. 4. Nyquist plots for S5d and S14d in Hank solution

For the equivalent circuit $R_{\text{sol}}$ is the solution resistance, $R_1$ is the resistance of the hydroxyapatitic layer, $Q_1$ is the constant phase element of the hydroxyapatitic layer and $W$ is Warburg resistance which is a diffusion element.

A true capacitive behavior is characterized by $n=1$. When $n$ is less than 1 a non-ideal capacitance interface is indicated [18].

Table 4

Electrochemical parameters of the equivalent circuits obtained after fitting results of EIS test for S5d and S14d in Hank solution after 5 and 14 days of immersion

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_{\text{sol}}$ / $\Omega$</th>
<th>$R_1$ / $\Omega$</th>
<th>$Q_1$ / $\Omega^{-1}$</th>
<th>$n_1$</th>
<th>$W$ / $\Omega$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S5d</td>
<td>350</td>
<td>29000</td>
<td>13.8 x 10$^{-6}$</td>
<td>0.550</td>
<td>-</td>
</tr>
<tr>
<td>S14d</td>
<td>40.2</td>
<td>20500</td>
<td>40.5 x 10$^{-6}$</td>
<td>0.328</td>
<td>35.7 x 10$^{-6}$</td>
</tr>
</tbody>
</table>

Fig.5. Circuits proposed: a) one time constant circuit for S5d and b) two time constants circuit for S14d
On the cyclic voltammetry curves for both studied samples, no breakdown phenomena were detected - as can be seen in Fig. 6.

![Cyclic voltammetry curves for S5d and S14d in SBF solution](image)

**Fig. 6. Cyclic voltammetry curves for S5d and S14d in Hank solution**

Furthermore, the cyclic voltammetry curve for CoCrMo sampled after it was immersed for 5 days in SBF solution indicates that, with increasing immersion time, the corrosion current density decreases, aspect attributed to the compactisation of the HA layer formed on the surface of the alloy.

### 4. Conclusions

With increasing time the contact angle is decreasing while the roughness is presenting an increase. From this result, it can be said that the sampled immersed for 14 days in SBF (S14d) is more hydrophilic than the one immersed for 5 days. Another plus than can be observed with increasing time is the smaller corrosion rate for the sample immersed for 14 days in SBF solution.

### Acknowledgements

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REFERENCES


[13] Lu-Ning Wang, Jing-Li Luo „Preparation of hydroxyapatite coating on CoCrMo implant using an effective electrochemically-assisted deposition pretreatment”, Materials characterization (6) 2, 2011, pp. 1076–1086


