STABILITATEA MASELOR FOSFATICE FLUORURATE
PE ALIAJE DE CoCrMo
ABOUT STABILITY OF ELECTRODEPOSITED FLUORIDATED PHOSPHATE
MASSES ON CoCrMo ALLOYS

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CoCrMo alloys are extensively used in tissue engineering in both dental and orthopaedic applications and are highly recommended due to the good ratio quality /price comparing with other metallic biomaterials. The present approach is related to electrodeposition of fluoridated phosphate masses with good ratio calcium to phosphorus close to the one existing in bone.

SEM and EDX analysis confirm that the electrochemical method for deposition of fluoridated apatite on CoCrMo is efficient and the results were quantified using electrochemical and mechanical measurements.

Keywords: CoCrMo alloys, electrochemical deposition, SEM, EDX, artificial saliva, physiological serum

1. Introduction

Having very good mechanical properties as castability, corrosion and wear resistance CoCrMo alloys [1] nowadays, are extensively used in tissue engineering in both dental and orthopaedic applications [2,3]. Even as heads in artificial joints. CoCrMo alloys have been introduced in bioapplications at the begging of the last century, but due especially to its problems with ion release for a period of time was used with limitations. A remarkable comeback was known in its using after introducing largely the surface engineering procedures [4,5] and the type of Ni-free alloy according to ASTM F-75 standard [6].

In medicine regeneration, CoCrMo alloys are highly recommended due to the good ratio quality /price and comparing with other metallic biomaterials as stainless steels [7] which have disadvantage in corrosion resistance or with titanium alloys which have demerit in wear resistance [2], despite the large variety of surface modifications proposed for enhancing their performance especially at the surface level [8].

The wear resistance of the CoCrMo alloys is due to its passive film formed at the surface in various bioliquids [10]. The existence of a small amount of nickel as an impurity, despite the fact International Agency for Research on Cancer (IARC) of the World Health Organization (WHO) estimates that nickel is carcinogenic [11], is able to maintain workability. More recently, taking into account the bacteria extension, and knowing the silver effect in enhancing antibacterial function new coatings having antibacterial inhibition effect were elaborated on the CoCrMo alloy surface [12] including hydroxyapatite (HA) as bioactive component and silver as antibacterian agent as well. Hydroxyapatite as bioactive coating was elaborated via various procedures [13,14] leading to various properties. It has been reported that plasma-sprayed HA coatings dissolve and degrade quickly, resulting in the weakening of the coating-substrate bonding or the implant fixation to the host tissues [15]. For this reason any changes to the HA that result in a higher chemical stability would be an advantage.

Impregnations to the HA crystal structure the chemical elements such as Fluoride by substituting OH− groups was performed successfully on various alloys [16,17].

The present approach is related to electrodeposition of fluoridated phosphate masses with good ratio calcium to phosphorus close to the

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one existing in bone, in order to provide resistance to dissolution. Firstly the aim of present research is trying to establish a relation between electrochemical behaviour of such coating from corrosion parameters in bioliquids and from ions release evaluation with mechanical properties. A comparison of electrochemical stability of the coated alloy in saliva and in physiological NaCl solution is discussed as well.

2. Experimental

For electrodeposition of phosphate masses were used samples of CoCrMo. Samples were polished on SiC abrasive papers (600, 800 and 1200) and after that etched in HF 4% for 2 minutes. For 15 minutes the samples were ultrasonicated in acetone and ethanol in order to remove particles from the SiC paper. Finally the samples were rinsed in distilled water and dried at the room temperature. The content of electrolyte solution was (NH₄)₂HPO₄ 0.025 M, NH₄F 0.012 M and CaCl₂·2H₂O 0.042 M, almost similar with the electrolyte used in literature for electrodeposition of fluoridated hydroxyapatite on stainless steel titanium [18]. A volume of H₂O₂ 3% was added in order to enhance the deposition process of dense coating by the release of H₂ gas and production of hydroxyl ions. The chemical composition of CoCrMo alloy it’s according to ASTM F75 [6].

2.1. Coating process

The coating process was performed at two different temperatures: 28°C (sample A) and at 22°C (sample B) using an electrochemical cell (Figure 1.) with a platinum plate as counter electrode (anode), Ag/AgCl as reference electrode and CoCrMo as working electrode (cathode). Working parameters are presented in Table 1. All the experiments were performed using a PGZ 301 potentiostat/ galvanostat controlled by a computer equipped with Volta Master 4 Software.

After electrodeposition all samples were calcinated at 400°C temperature for 1 hour. Thermal treatment was made in order to increase the crystallinity and the purity of the coated CoCrMo samples. Calcination was also, beneficial for strengthening the bonds ofapatite coatings. Figure 2 shows variation of potential in time of electrochemical deposition of fluoridated apatite coatings on CoCrMo samples.

![Electrolytic cell scheme used in coating process](image1.png)

**Fig. 1 - Electrolytic cell scheme used in coating process:** 1-WE (CoCrMo), 2-RE (Ag/AgCl), 3-CE (Pt), 4-electrolyte, 5-potentiostat/ galvanostat, 6-magnetic stirrer, 7-stirrer/ Schema celulei electrochimice folosite în procesul de depunere: 1-EL (CoCrMo), 2-ER (Ag/AgCl), 3-CE (Pt), 4-soluție electrolit, 5-potențiostat/ galvanostat, 6-agitațor magnetic, 7-agitațor.

![Coating process](image2.png)

**Fig. 2 - Coating process/ Procesul de depunere.**

Curve equations for coating process are shown below: equation (1) for coated CoCrMo at 28°C have standard deviation, R² = 0.65 and the second equation (2) for coated CoCrMo at 22°C have standard deviation, R² = 0.92

\[
y = -0.80368 + 0.1388 \cdot e^{0.07442t}
\]

\[
y = -0.88625 + 0.43206 \cdot e^{-0.02516t}
\]

The mechanism of electrolytic deposition can be described as a series of electrochemical reactions.

**Table 1**

<table>
<thead>
<tr>
<th>CoCrMo Sample/ Proba CoCrMo</th>
<th>Current Density/ Densitate de curent [mA/cm²]</th>
<th>Electrodeposition time/ Timp de electrodepunere [min]</th>
<th>Deposition temperature/ Temperatura de depunere [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-1</td>
<td>60</td>
<td>28</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td></td>
<td>22</td>
</tr>
</tbody>
</table>
The possible sources of OH⁻ at the cathode are [19]

\[
\begin{align*}
O_2 + 2H_2O + 4e^- & \rightarrow 4HO^- \\
NO_3^- + H_2O + 2e^- & \rightarrow 2HO^- + NO_2 \\
2H_2O + 2e^- & \rightarrow H_2 + 2HO^- 
\end{align*}
\]

Hydroxide ions, generated during the electrodeposition process, resulted in an increase of the pH in the vicinity of the cathode; which led to the occurrence of the following reactions:

\[
\begin{align*}
H_2PO_4^- + e^- & \rightarrow HP0_3^{2-} + \frac{1}{2}H_2 \\
H_2PO_4^- + 2e^- & \rightarrow PO_3^{3-} + H_2 \\
H_2PO_4^- & \rightarrow HPO_3^{2-} + H^+ \\
HPO_3^{2-} & \rightarrow PO_4^{3-} + H^+ 
\end{align*}
\]

The precipitation of phosphate ions occurred due to the acid-base reactions, which are vital for the crystallization process of formation of FHA coating film according to the following reaction:

\[
H_2PO_4^- + HO^- \rightarrow HPO_4^{2-} + H_2O 
\]

The suitable local chemical environment in the vicinity of the cathode enabled the HPO_4^{2-} ions to react with the Ca^{2+} ions [17].

\[
\begin{align*}
Ca^{2+} + HPO_4^{2-} + H_2O & \rightarrow CaHPO_4 \cdot 2H_2O \\
Ca_{10}(PO_4)_6(OH)_2 + 4PO_4^{3-} + 10H^+ & \rightarrow 10CaHPO_4 + 2HO^- \\
(10 - x)Ca_{2+} + (6 - x)PO_4^{3-} + xHPO_4^- + (2 - x)HO^- & \rightarrow Ca_{10 - x}(HPO_4)_x(PO_4)_{6 - x}(OH)_{2 - x} 
\end{align*}
\]

where 0 < x ≤ 2.

Addition of NaF into the electrolyte led to the occurrence of the following reactions. At the early stage, Ca^{2+} ions rapidly consumed the F⁻ ions in the electrolyte to form CaF_2 which can be expressed as follows [20]

\[
\begin{align*}
Ca_{3}(PO_4)_3OH + 10F^- + (7 - n)H^+ & \rightarrow 5CaF_2 + H_2O + (3 - n)H_2PO_4^- + nHPO_4^{3-} \\
5CaF_2 + H_2O + (1 - x)H_2O & \rightarrow Ca_{2}(PO_4)_3(3OH)_{1 - x}F_x + (10 - x)F^- + (7 - x - n)H^+ \\
\text{where} & \text{ (0 < x < 1, 0 < n < 3)} 
\end{align*}
\]

Combining reactions (15) and (16) resulted in the formation of FHA via the following reaction:

\[
10Ca_{2+} + 6PO_4^{3-} + xF^- + (2 - x)HO^- \rightarrow Ca_{10}(PO_4)_6F_x(3OH)_{2 - x} 
\]

3. Results and discussions

3.1. X-Ray Diffraction Analysis

X-Ray Diffraction analysis was performed for the coated samples of CoCrMo at 22°C with Empyrean PANalytical Diffractometer with radiation Cuα (λ=1.5406Å). The acquisition was done from 10 to 80 degrees with 0.02 degree step and acquisition time with 2 seconds step. Incidence angle was 1 degree. In Figure 3 is presented XRD analysis for coated CoCrMo samples.

From the XRD analysis it can be observed the deceleration of the mineralogical crystalline phases of fluorohydroxyapatite and CaHPO_4.

3.2. Scanning electron microscopy analysis

Coated samples of CoCrMo alloy were investigated with a scanning electron microscope HITACHI, S-2600N Model coupled with energy-dispersive X-ray spectroscopy (EDX) for morphology determinations. In Figure 4 are presented images with SEM characterization.

The coating, after alkaline treatment, was converted to HA according to the following reaction:

\[
10CaHPO_4 + 2HO^- \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 4PO_4^{3-} + 10H^+ 
\]

Calcium deficient hydroxyapatite was formed as follows [20]

\[
(10 - x)Ca_{2+} + (6 - x)PO_4^{3-} + xHPO_4^- + (2 - x)HO^- \rightarrow Ca_{10 - x}(HPO_4)_x(PO_4)_{6 - x}(OH)_{2 - x} 
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\]

The difference between coated CoCrMo at 28°C and the coated CoCrMo at 22°C shows a better adherence on the metallic substrate and a more uniform deposition for the electrochemical deposition carried at 22 degrees.
Fig. 4 - SEM images of apatite coatings: a), b) Coated CoCrMo at 28°C; c), d) Coated CoCrMo at 22°C. Imagini SEM depuneri apatite: a), b) CoCrMo acoperit la 28°C, c), d) CoCrMo acoperit la 22°C.

Fig. 5 - EDX spectra of apatite coatings: a) Coated CoCrMo at 28°C; b) Coated CoCrMo at 22°C. Spectrul EDX: a) CoCrMo acoperit la 28°C; b) CoCrMo acoperit la 22°C.

Fig. 6 - Tafel plots for coated and uncoated CoCrMo alloy. Curbele Tafel pentru aliajul CoCrMo.

Figure 5 shows EDX spectra of coated CoCrMo samples and permit the calculation of molar raports Ca/P.

The EDX spectra analysis revealed the presence of calcium and phosphorus, but also the presence of ions substrate, cobalt, chromium and
molybdenum. Molar ratios of phosphate masses of coated CoCrMo alloy are 1.40 for coated CoCrMo at 28°C and 1.88 for coated CoCrMo at 22°C.

EDX analyses shows that CoCrMo sample coating at 28°C is a little bit deficient in calcium, but CoCrMo sample at 22°C is easily overcome in calcium, being much closer to the molar raport Ca/P in bones. Next determinations for characterization of the coated CoCrMo were performed on coated CoCrMo at 22°C.

3.3. Stability of CoCrMo coated with phosphate masses in saline solution and artificial saliva

3.3.1. Electrochemical characterization

Application of fluoridated hydroxyapatite (FHA), $\text{Ca}_{10}\left(\text{PO}_4\right)_6(\text{OH})_2\text{F}$, where $0 < x < 2$ is the degree of fluoridation (FHA) in comparison with HA coating, could provide better stability as can be seen from electrochemical data and ions release determinations.

CoCrMo samples and coated CoCrMo samples were characterized in saline solution (NaCl 0.9% wt %) and in artificial saliva by electrochemical methods, such as Tafe plots, electrochemical impedance spectroscopy and cyclic voltammetry. The chemical composition of artificial saliva Afnor is presented in Table 2.

**Tafel plots**

The Tafel plots determination were carried in the interval – 200/+200 mV in reference to open circuit potential and with a scan rate of 2mV/seconds. The determinations were performed using the same three electrodes system as the system used for coating process using artificial saliva and psysiological serum (NaCl 0.9% wt%) as electrolytes.

The polarization curves obtained by VoltaMaster 4 Software are presented in Figure 6.

The smallest current density values (Table 3) were recorded in case of coated CoCrMo alloy immersed in artificial saliva, but in both solutions the coated alloy has a good corrosion resistance.

According to obtained data from Tafel plots it is obvious that corrosion rate is smallest in case of coated alloy and we can confirm that the coverage with fluoridated phosphate masses improve the anticorrosion properties.

The corrosion rates are lower when the alloy is coated and in saline solution are higher than in artificial saliva, the latter being less aggressive. Polarization resistances are enhanced by phosphate masses and corrosion potentials values are displaced from electronegative to electropositive domain, indicating a possible passive character.

As far as the bioactivity is concerned, porosity is a crucial parameter, since it influences the interactions at the implant host tissue interface, especially the reaction rate. A porous coating allows a deeper penetration of cells inside the biomaterial, and thus higher levels of cell attachment can be reached [22]. Porosity can also be a way to tune the stiffness of a material, as it happens for natural bones [23]. In this way, it is possible to reduce the stiffness of biomedical materials, to match that of natural bone tissue, thus limiting the so-called “stress shielding” effect [24].

The surface porosity fraction for FHA was estimated by potentiodynamic polarization using the following equation:

$$\rho = \frac{R_p}{R_p^0} \times 10^{\left(\frac{\Delta E_{corr}}{10}\right)}$$

(18)

Where $R_p$ and $R_p^0$ are the polarization resistances of the bare substrate and the coating/substrate pair, respectively, $\Delta E_{corr}$ is the potential difference between them, and $\beta$ is the anodic Tafel coefficient of the substrate.

The calculated values of the coating porosity from the potentiodynamic analyses are listed in Table 2.

The coating protective efficiency (Pi) can be calculated using the using the following equation [25]:

$$P_i = 100 \times \left(1 - \frac{R_p^0}{R_p}\right)$$

(19)

Where $R_p^0$ and $R_p$ are the polarization resistances of the uncoated/substrate coated bare substrate. The protective efficiency calculated for equation 19 is shown in Figure 7.

FHA coating showed a higher protective efficiency in physiological serum than in artificial saliva. It can be seen that the corrosion rate of CoCrMo improved, after FHA coating. FHA inhibits the corrosive action of the artificial saliva or physiological serum from penetrating into the substrate. FHA coating reduce the diffusion of the corrosive medium into the substrate and hence, decline the corrosion rate.

![Fig. 7 - Protective efficiency](image)
Chemical composition of artificial saliva Afnor/ Compoziția chimică saliva artificială Afnor

<table>
<thead>
<tr>
<th>Substance</th>
<th>NaCl</th>
<th>KCl</th>
<th>Na₂HPO₄</th>
<th>NaHCO₃</th>
<th>KSCN</th>
<th>CH₃COON₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quantity (g/L)</td>
<td>0.7</td>
<td>1.2</td>
<td>0.26</td>
<td>1.5</td>
<td>0.33</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Table 2

Electrochemical parametres from Tafel plots/ Parametri electrochimici din curbele Tafel

<table>
<thead>
<tr>
<th>Electrodes</th>
<th>Artificial saliva (Afnor)</th>
<th>Physiological serum (NaCl 0.9%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>i_{corr} [µA/cm²]</td>
<td>CoCrMo</td>
<td>CoCrMo/FHA</td>
</tr>
<tr>
<td>-0.481</td>
<td>0.099</td>
<td>0.546</td>
</tr>
<tr>
<td>Ec_{corr} [V]</td>
<td>10.63·10⁻²</td>
<td>21.72·10⁻¹</td>
</tr>
<tr>
<td>R_{p} [Ω/cm²]</td>
<td>2.96·10⁻¹</td>
<td>1.139·10⁻³</td>
</tr>
<tr>
<td>V_{corr} [mm/Y]</td>
<td>-</td>
<td>13.41</td>
</tr>
</tbody>
</table>

Table 3

Fig. 8 - Nyquist diagrams for CoCrMo and coated CoCrMo in artificial saliva and in saline solution/ Diagramele Nyquist pentru CoCrMo acoperit și neacoperit în soluție de salvă artificial și soluție salină

Fig. 9 - Bode diagrams for CoCrMo and coated CoCrMo in artificial saliva and in saline solution/ Diagramele Bode pentru CoCrMo acoperit și neacoperit în soluție de salvă artificial și soluție salină.
**Electrochemical Impedance Spectroscopy**

The Electrochemical Impedance Spectroscopy (EIS) determinations were performed using working parameters for initial frequency 100 KHz, final frequency 50 MHz and 10mV amplitude. The three electrodes system was the same: Ag/AgCl, Pt, CoCrMo and CoCrMo coated.

Figure 8 present Nyquist diagrams for coated and uncoated CoCrMo in artificial saliva and in saline solution.

Figure 9 present Bode diagrams for coated and uncoated CoCrMo in artificial saliva and in saline solution.

Electrochemical parameters from electrochemical impedance spectroscopy determinations are presented in Table 4, where Rsol (R1) is solution resistance, Rp (R2) is load transfer resistance (polarisation resistance at CoCrMo/ electrolyte interface), CPE1 is constant phase element (electric double layer capacitance at the interface CoCrMo/ electrolyte) and CPE2 is constant phase element of the coating/ electrolyte interface.

The EIS results indicated that the CoCrMo surface is composed of a bi-layered oxide consisting of an inner barrier layer associated to high impedance and responsible for corrosion protection, and an outer porous layer of lower impedance, which can sustain a suitable behaviour in bioapplication, including cell adhesion.

**Table 4**

<table>
<thead>
<tr>
<th>Solutions/ Soluții</th>
<th>Artificial saliva/ Saliva artificială</th>
<th>Saline Solution/ Soluție salină</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Electrodes</strong></td>
<td>CoCrMo</td>
<td>CoCrMo/FHA</td>
</tr>
<tr>
<td><strong>Electric circuit</strong></td>
<td></td>
<td>CoCrMo</td>
</tr>
<tr>
<td>Rsol (R1) [Ω/cm²]</td>
<td>29.70</td>
<td>119.31</td>
</tr>
<tr>
<td>Rp (R2) [Ω/cm²]</td>
<td>11.54·10⁻²</td>
<td>27.52·10⁻²</td>
</tr>
<tr>
<td>CPE₁</td>
<td>1.0·10⁻⁹</td>
<td>10.93·10⁻⁹</td>
</tr>
<tr>
<td>n₁</td>
<td>0.91</td>
<td>0.91</td>
</tr>
<tr>
<td>CPE₂</td>
<td>-</td>
<td>50.34·10⁻⁹</td>
</tr>
<tr>
<td>n₂</td>
<td>-</td>
<td>0.48</td>
</tr>
</tbody>
</table>
In both cases, in physiological serum and in artificial saliva, the coating layer improves the resistance of the substrate (Rp values). Also Rp values are correlated with values obtained from Tafel plots. In artificial saliva, both studied materials covered and uncovered, shows a better corrosion resistance compared to physiological serum. Can be noticed that in case of CoCrMo/physiological serum the Rp value is with an order of magnitude smaller than the CoCrMo/ artificial saliva, indicating a much more aggressive character of the serum. From the values of n1 and n2 we can say that at the interface of the CoCrMo/ electrolyte exist a capacitive character and at the interface of CoCrMo/FHA/electrolyte we have a diffusive character through obtained porous layer.

Cyclic Voltammetry
For cyclic voltammetry determinations the working parameters were: \( E_0 = -800 \text{mV}, \ E_1 = -800\text{mV}, \ E_2 = 1500 \text{ mV} \) and scan rate 2mV/seconds. In Figure 10 are shown cyclic voltammetry curves for uncoated and coated CoCrMo samples in solutions, artificial saliva and physiological serum. All electrochemical characterizations confirm that the phosphate masses coating has improved corrosion resistance. Regarding the aggression of the solutions studied the results led to the fact that that saline solution has a more aggressive character due to free \( \text{Cl}^- \) ions in solution, which causes a stronger corrosion.

3.3.2. \( \text{Ca}^{2+} \) ion release in saline solution (NaCl 0.9%)
Calcium ions release on coated CoCrMo sample obtained at 22\(^\circ\)C in saline solution is presented in Figure 11 together with an empirical model of dissolution at interface. The observation time was until 100 hours and it is to mention that the evolution in time represents a trend to steady state.

3.4. Contact Angle measurements
The determination of contact angle was performed with CAM 100 Equipment. The procedure supposes to place an equal volume (drop) of distilled water on samples surface. In Figure 12 the values represent the average from 5 determinations. For all uncoated CoCrMo the contact angle values are bigger than 95\(^\circ\) and the average is 96.3\(^\circ\) which indicate a hydrophobic character.
In case of CoCrMo with fluoridated phosphate masses coating the average for contact angle is 15.3 fact that puts in evidence the superhydrophilic character. The hydrophilicity is in relation with biocompatibility and for small contact angles the biocompatibility is higher.

3.5. Microhardness and Adherence tests
The Vickers test used for Microhardness determinations of metallic materials was performed with Buehler equipment by applying a load of 200 g for 10 seconds and was expressed by using the Vickers units (µHV).
The obtained value for coated CoCrMo alloy was 469 HV. Comparing with the standard value 310 HV according to ASTM F75, the obtained value is higher and indicates better hardness due to the coating layer.
Adhesion of studied coatings was determined according to ASTM D4511 with a device for determining the adhesion type PosiTest Pull-off adhesion AT-A (DeFelsko, USA).
Protective coating adhesion was evaluated by determining the highest pullout strength (pull-off Strength) which is required for detach a dolly attached with adhesive coating. This dolly (10mm diameter) was closely related to the sample’s surface covered with epoxy resin adhesive in two components (epoxy-patch-907 Hysol Loctite / Henkel). The adhesive was allowed to strength for 72 hours at room temperature. Tests were made with the speed of 0.875 MPa.
By comparison the literature data of the adherence tests [26], the obtained values for coated CoCrMo samples are modest (2.79 MPa and 2.69 MPa), probably due to the fact that the coating layer was not uniform.

4. Conclusions
SEM and EDX analysis confirm that the electrochemical method for deposition of phosphate masses on CoCrMo is efficient. X-Ray Diffraction analysis proves the existence of mineralogical crystalline phases of fluorhydroxyapatite and CaHPO\(_4\) as well.
An efficiency evaluation was quantified using electrochemical and mechanical measurements and we found that fluoridated phosphate masses electrodeposited on CoCrMo alloy is more stable in both electrolyte artificial saliva and physiological NaCl solution respectively.
The mechanical properties meaning microhardness and adherence are better for nanosized coatings as well.

Acknowledgements

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