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INVESTIGATION ABOUT THE ABILITY TO BUILD PHOSPHATES ON CoCrMo

Sabina GRIGORESCU[1], Daniela IONIȚĂ[2], Ioana DEMETRESCU[3]

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 Cr_2O_3 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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[1] PhD student, Department of General Chemistry, University POLITEHNICA of Bucharest, Romania, e-mail: grigorescusabina@yahoo.com

[2] As. Prof. PhD., Department of General Chemistry, University POLITEHNICA of Bucharest, Romania, Corresponding author

[3] Prof., Department of General Chemistry, University POLITEHNICA of Bucharest, Romania, Corresponding author

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 160^0C 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 300^0C 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 90^0C. The second step of the heat treatment was performed at 450^0C for 3 hours in air.

After these, the plates were immersed in 96 ml of SBF solution at 36.5^0C 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 1

Ionic concentration

Concentration (mmol/dm^3)								
	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	HCO_3^-	HPO_4^{2-}	SO_4^{2-}
SBF	142.0	5.0	1.5	2.5	147.8	4.2	1.0	0.5

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 Gwyddion software.

2.3.2 Contact angle measurements

In order to characterize the wettabilitty 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 Spectometer 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; $NaHCO_3$ – 0.35; $NaH_2PO_4 \cdot H_2O$ – 0.25; $Na_2HPO_4 \cdot 2H_2O$ – 0.06; $CaCl_2 \cdot 2H_2O$ – 0.19; $MgCl_2$ – 0.19; $MgSO_4 \cdot 7H_2O$ – 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} – 10^5 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).

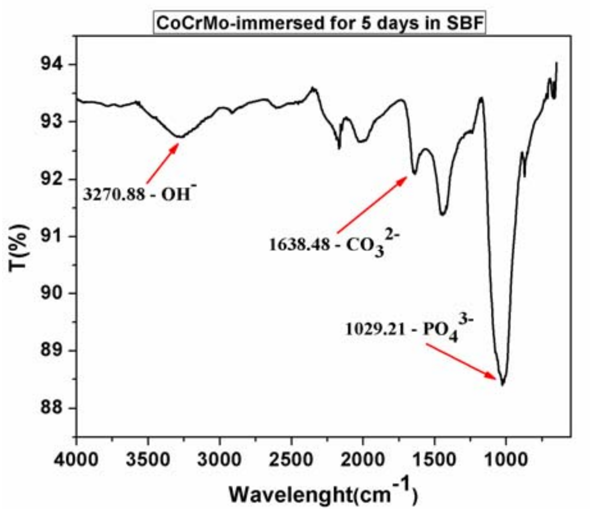

Fig . 1. FTIR spectrum of S5d

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 Table2.

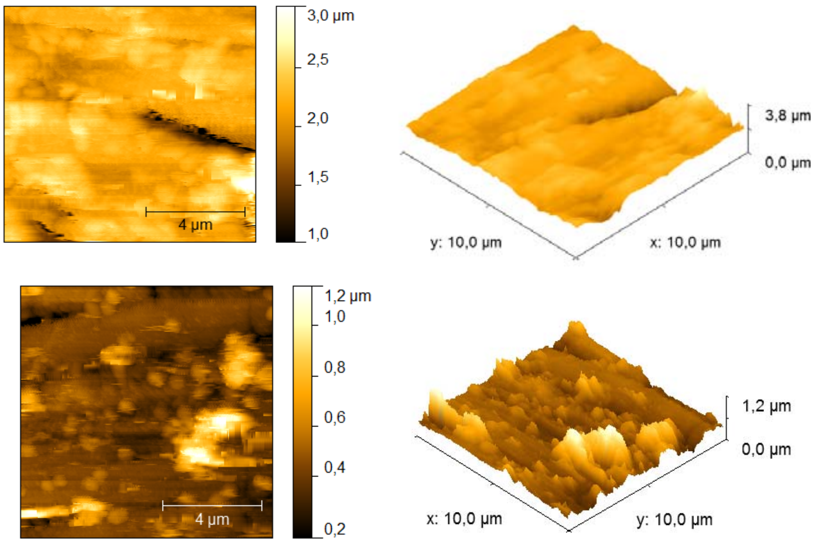

Fig. 2. AFM images for S5d and S14d

Table 2

Ra and contact angle values after 5 and 14 days of immersion in SBF (S5d and S14d)

Sample	**R_a(µm)**	**Contact angle(°)**
S5d	0.120	77.46
S14d	0.179	56.69

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_{cor}), corrosion current (i_{cor}) and rate of corrosion (v_{cor}). 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_{cor}, 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

Comparison of corrosion parameters for: S5d and S14d

Sample	**E_{corr} (V)**	**j_{corr} (A/cm^2)**	**v_{corr} (mm/year)**
S5d	-0.34617	4.77×10^{-6}	$0.440\ 10^{-4}$
S14d	-0.02208	$2.23\ 10^{-6}$	$0.203\ 10^{-4}$

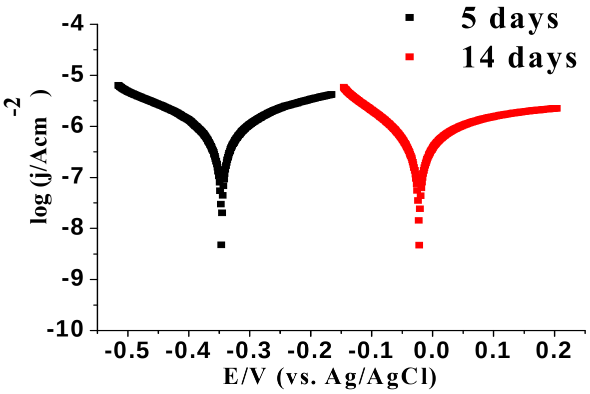

Fig. 3. Tafel plots for S5d and S14d , in Hank solution

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 contant 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.

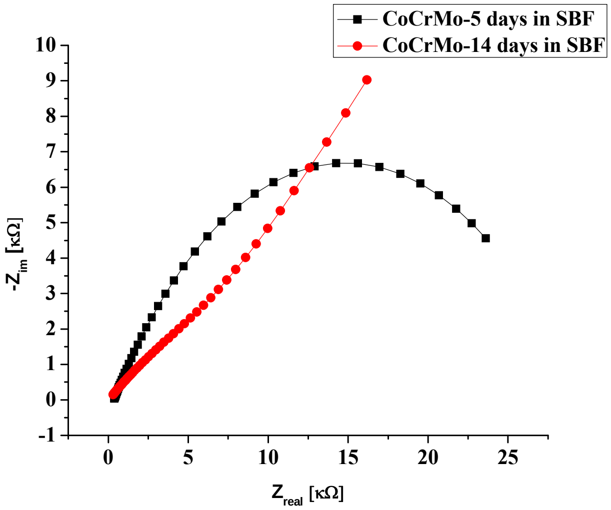

Fig . 4. Nyquist plots for S5d and S14d in Hank solution

For the equivalent circuit R_{sol} is the solution resitance, 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 witch 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

Sample	**R_{sol} / Ω**	**R_1 / Ω**	**Q_1 /$Ω^{-1}$**	**n_1**	**W**
S5d	350	29000	13.8 x10^{-6}	0.550	-
S14d	40.2	20500	40.5 x10^{-6}	0.328	35.7 x 10^{-6}

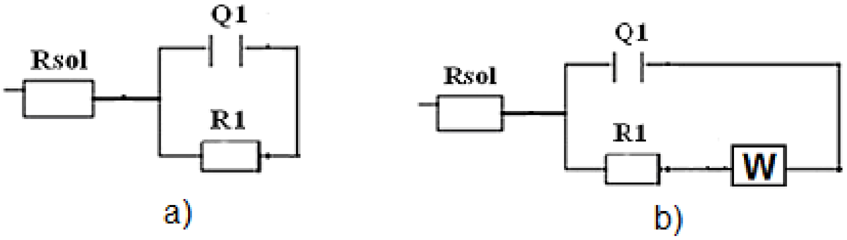

Fig.5. Circuits proposed : a) one time constant circuit for S5d and b) two time constants circuit for S14 d

On the cyclic voltammetry curves for both studied samples, no breakdown phenomena were detected - as can be seen in Fig.6.

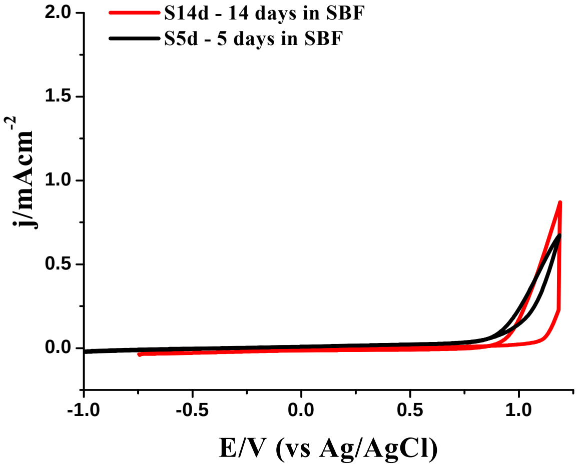

Fig. 6. Cyclic voltammetry curves for S5d and S14d in Hank solution

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.

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REFERENCES

[1] *J. Ohnsorge, R. Holm,*"Surface investigations of oxide layers on cobalt-chromium-alloyed orthopedic implants using ESCA technique",Med. Prog. Technol. 1978 23;5(4):171-7

[2] *H.S. Dobs, J.L. Robertson, J. Mater,*" Heat treatment of cast Co-Cr-Mo for orthopaedic implant use" ,Journal Materials Sci. 1983,18(2),pp 391-401

[3] *L. C. Lucas, R. A. Buchanan, J. E. Lemons and C. D. Griffin,"* Susceptibility of surgical cobalt-base alloy to pitting corosion", J. Biomed. Mater.Res, 16(4), 1982, pp 799-810

[4] *A.W. Hodgson, B. MiscVon Rechenberg, S. Virtanen,"* An analysis of the in vivo deterioration of Co-Cr-Mo implants through wear and corrosion", Proc Inst Mech Eng H. 2007;221(3):291-303

[5] *I. Milošev, H.-H. Strehblow,*" The composition of the surface passive film formed on CoCrMo alloy in simulated physiological solution", Electrochimica Acta, 48(19),2003, pp. 2767-2774

[6] A.W.E. Hodgson, S. Kurz, S. Virtanen, V. Fervel, C.-O.A. Olsson, S. Mischler," Passive and transpassive behaviour of CoCrMo in simulated biological solutions", *Electrochimica Acta,49(13),2004,pp. 2167-2178*

[7] *J.J. Jacobs, J.L. Gilbert, R.M. Urban,"* Corrosion of Metal Orthopaedic Implants", *J Bone Joint Surg Am.* 1998;80:268-82

[8] *M.A. Germain, A. Hatton, S. Williams, J.B. Matthews, M.H. Stone, J. Fisher, E. Ingham,*" Comparison of the cytotoxicity of clinically relevant cobalt chrome and alumina ceramic wear particles *in vitro*" Biomaterials,2003, 24(3), pp 469-479

[9] *Y. Okazaki, E. Gotoh,"* Comparison of metal release from various metallic biomaterials in vitro", Biomaterials 26 (1),2005, pp 11-21

[10] *A. Masse, M. Bosetti, C. Buratti, O. Visentin, D. Bergadano, M. Cannas,*" Ion release and chromosomal damage from total hip prostheses with metal-on-metal articulation", Journal of Biomedical Materials Research. Part B: Applied Biomaterials 67B (2003),pp 750-757

[11] *J.H. Dumbleton, M.T. Manley,*" Metal-on-Metal total hip replacement: what does the literature say?", Journal of Arthroplasty 2005;20(2):174-88

[12] *T. Hanawa,*" Metal ion release from metal implants", Materials Science and Engineering C 24 (2004) :745-752

[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

[14] *D.Ionita , I. Man, I. Demetrescu* " The behaviour of electrochemical deposition of phosphate coating on CoCr Bio alloys "Key Engineering Materials (2007), 330-332 , pp. 545-548

[15] *Grandfield K, Palmquist A, Gonçalves S, Taylor A, Taylor M, Emanuelsson L, Thomsen P, Engqvist H* , "Free form fabricated features on CoCr implants with and without hydroxyapatite coating in vivo: a comparative study of bone contact and bone growth induction " , J Mater Sci Mater Med. 22(4), 2011,pp. 899-906.

[16] *M Sovar, C. Ducu, D. Iordachescu I Demetrescu* , "Stability of bioactivated Co-Cr alloys in biological environment ", Key Engineering Materials 361-363,2008, pp.737-740

17] *Bocardo, J.C.E Heredia, M.A.L. Hernandez, D.A.C Ramirez, A.M. Robles*, "Apatite Formation on Cobalt and Titanium Alloys by a Biomimetic Process" , Advance in Technology of Materials and Materials Processing Journal, 7, 2005, 141-148

[18] *V.S.Saji, H. C. Choe, W. A. Brantley*, " An electrochemical study on self-ordered nanoporous and nanotubular oxide on Ti-25Nb-5Ta-7Zr alloy for biomedical applications", Acta Biomaterialia 5, 2009, pp. 2303-2310