BIOMIMETIC CALCIUM PHOSPHATE COATING OF CoCr ALLOYS

Mariana Prodana[1], Florentina Golgovici[1], Andrada Negru[2], Marius Enachescu[1]*
[1]Center for Surface Science and Nanotechnology,
University "Politehnica" of Bucharest, 060042, Bucharest, Romania
[2]University of Pitesti, 110040, Pitesti, Romania
*e-mail: marius.enachescu@upb.ro

Abstract. CoCr aloys are most common material used as implantable material because of it reduced cost and good mechanical properties. This work presents our results of obtaining biomimetic calcium phosphate coating of CoCr and to characterize the properties of such coatings. The coating was prepared by immersing the CoCr substrates into the simulated body fluid (SBF) containing Ca^{2+} ions in sealed plastic bottles, kept at room temperature for one, fourteen and twenty one days. Detailed characterization including chemical, structural and morphological characterization (SEM, EDS, X-ray diffraction) were perfomed. ICP/MS (inductively coupled plasma mass spectrometer) determinations sustain chemical results put in evidence by Fourier Transformed Infrared Spectroscopy (FTIR), the ions release being much smaller for phosphate coatings formed after longer immersion time in SBF. The hydrophilic/hydrophobic character of the coatings was put in evidence by contact angle measurements (CA).

1. Introduction

Recently, there is a great interest in developing good coatings for implantable alloys that possess low cost and good mechanical properties. Osseointegration of metallic implants in bone is crucial for successful long-term treatment with ceramic prostheses in hip and knee arthroplasty. Cobalt chromium based alloys have remarkable mechanical and tribological properties being considered as the material of choice by some authors [1-3].

Different routes that simulate the bone healing of alloys implants have been evaluated in the last periods of times. Coatings such as hydroxyapatite (HA/ $Ca_{10}(PO_4)_6(OH)_2$) [4,5] has been used as bioactive coating due to the presence of Ca and P elements existing in the inorganic part of the bone [6-9].

Coating metallic implant as hydroxyapatite (HA) or other calcium phosphates with mimetic features of natural bone may reduce metallic ion release acting as a barrier against corrosion in biological media and accelerate the bone formation on the initial stage of osseointegration [10-14]. It is known that hydrophilic/hydrophobic balance may affect the bio performance results as well.

2. Material and methods

2.1. Materials

In the present study, CoCr alloy samples with the chemical composition given in Table 1 were used. Rectangular specimens 10×10×1 mm in size were cut from a CoCr plate. The pretreatment procedure was that specimens were mechanically polished, cleaned by HF/HNO_3 solution, rinsed with ethanol and deionised water, and subsequently air-dried. The group numbers of the specimens were assigned to the different processing conditions as flows: S1 –CoCr alloy immersed for one day in SBF as a control; S2- CoCr alloy immersed for fourteen days in SBF and S3- CoCr alloy immersed for twenty one days in SBF.

The chemical composition of SBF is as following: NaCl 8,367255g; $NaHCO_3$ 5,534g; $Na_2HPO_4.2H_2O$ 22,165g; $MgCl_2.6H_2O$ 0,51359g; $CaCl_2.2H_2O$ 0,51891g; Na_2SO_4 0,071 for 1 liter of deionized water;

Table 1. Chemical composition of cobalt–chromium alloy

Composition	Percentage amount
Chromium	29.00–31.00
Molybdenum	4.50–6.00
Silicon	0.70–1.30
Manganese	0.50–1.00
Carbon	0.40–0.50
Cobalt	60.0–64.5
Iron, nickel, nitrogen	Traces

2.2. Methods

SEM and EDAX analysis: The microstructure of the hybrid ceramic material was studied by scanning electron microscopy (SEM) using a Hitachi SU8230 Microscope equipped with EDX (Energy Dispersive X ray).

Spectroscopic measurements: the chemical bonds of new hybrid composite material were studied by FTIR which were performed with ATR Perkin-Elmer equipment.

CA investigations: The hydrophilic/hydrophobic balance was evaluated with the contact angle meter CAM 100.

ICP-MS determination: For Co^{2+} and Cr^{2+} ions release determination, an ELAN DRC-e inductively plasma mass spectrometer was used (ICP-MS). All samples (typically: 0.1–1.2 mg) were digested in 100 mL concentrated nitric acid (ULTRAPURE, Fa. Merck). Acid digestion was performed in a well determined volume of HNO_3 65%; after digestion, the samples were diluted 100 times and liquid fractions were analyzed.

XRD analysis: The composition and structure of the films formed on Co-Cr alloys were studied by X-ray diffraction (XRD) technique utilizing a SmartLab X-ray diffractometer (Rigaku, Japan) at 45 kV voltage, 200 mA, with a Cu target; the scanning rate was 5°/min with a step size of 0.01°.

3. Results and discussion

3.1. Spectroscopic analysis and morphology characterization of CoCr alloys

Surface morphology, structural and elemental analysis of coating, composition of calcium phosphate formed on the CoCr alloys were studied using the scanning electron microscope (SEM) described above, i.e., Hitachi SU8230 equipped with EDX at 10kV.

From figure 1 we can see the surface of CoCr alloy with some linear scratches that are specific for metallic sample because of the direction of polishing. On the metallic sample we can see some deposit of NaCl, fact that is confirmed by EDX analysis.

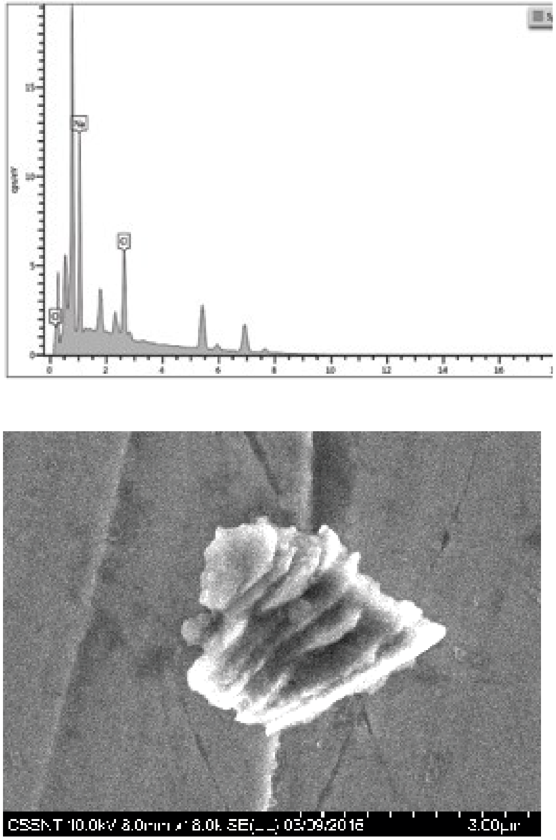

Figure 1. EDXS (top) and SEM (bottom) morphologies of Sample S1

In figure 2 we obtain on the surface of sample S2 morphology like a dandelion flower. From elemental analysis the Ca/P ratio is almost 1, that is specific for brushite ($CaHPO_4{\cdot}2H_2O$) which is a precursor of hydroxyapatite in bones and teeth, with an important role in bones mineralization. Peaks specific for metallic support appears in the spectra because the layer of brushite is not very dense and homogenous.

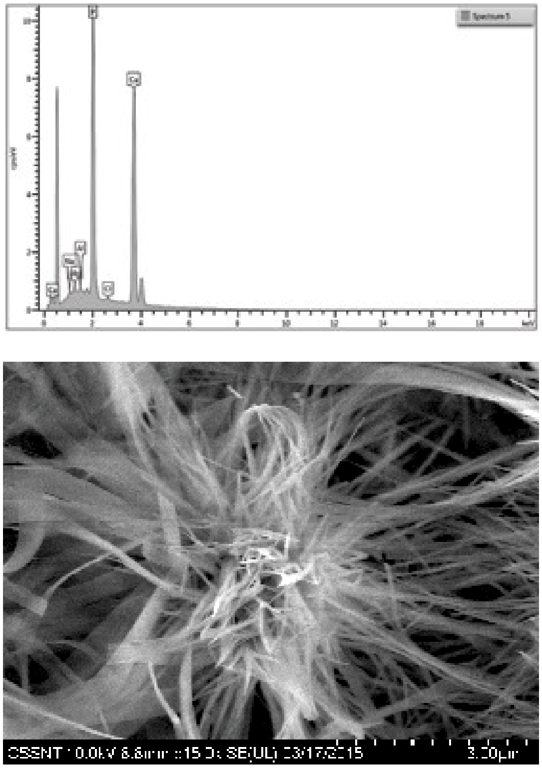

Figure 2. EDX (top) and SEM (bottom) morphologies of Sample S2

In figure 3 we observe the morphology of hydroxyapatite. We obtained a quantitative results with a Ca/P ratio of 1.67, fact that is confirmed from X-ray diffraction analysis.

The composition and crystalline structure of the films were studied by X-ray diffraction (XRD) technique. The XRD pattern for films deposited on CoCr alloys immersed in SBF solution at room temperature for 21 days are shown in figure 4. The patterns of the film formed on metallic surface indicate the presence of hydroxyapatite film.

The major peaks in figure 4 were observed at 2θ values of 31.77°, 32.19° and 32.91° corresponding to (-161), (-222) and (-360) planes of hydroxyapatite phase (according to ICDD File 00-076-0694). The XRD patterns of our samples is in good agreement with the literature data.

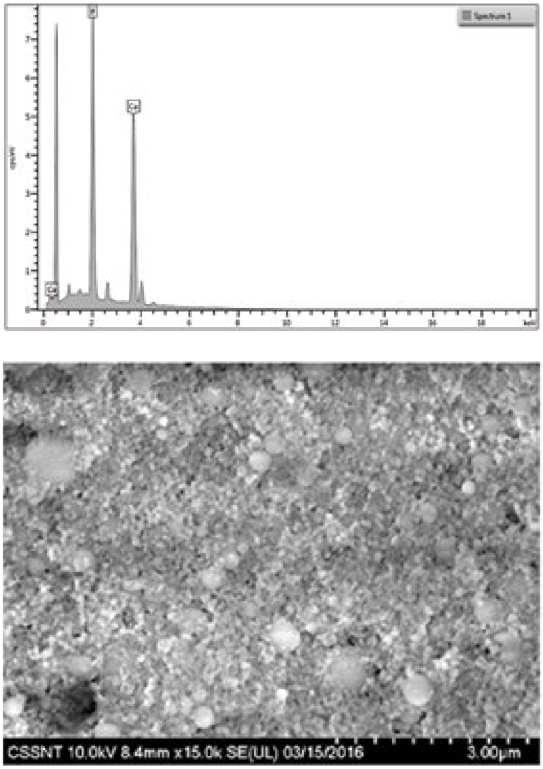

Figure 3. EDX (top) and SEM (bottom) morphologies of hydroxyapatite-sample S3

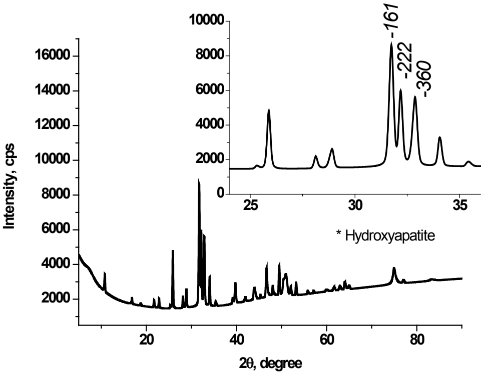

Figure 4. X ray diffraction spectra for sample S3

3.2 FTIR measurements

Sample S3 was analyzed using FTIR and infrared Spectral data.

In the literature, FTIR spectrum of HA coating present peaks at 3453 cm^{-1} and 1640 cm^{-1}. These peaks were identified that are due to the stretching and bending modes of absorbed water [15].

The stretching and bending vibration modes of hydroxyl group were identified at 3270 cm^{-1} and 634.23 cm^{-1}, respectively. PO_4^{3-} stretching and bending modes were seen at 560.13 cm^{-1}, 960 cm^{-1}, 042.71 cm^{-1}, 1099.33 cm^{-1} [16].

This presence confirms the formation of a well crystallized apatite structure. The carbonate band was observed at 1640 cm^{-1}. The peak observed at 2354 cm^{-1} could be assigned to adsorbed carbon dioxide [17].

In figure 5 is present our obtained spectra for CoCr/HA-sample S3.

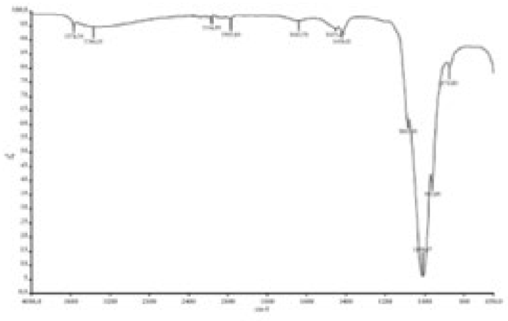

Figure 5. FTIR spectra of sample S3

3.3 CA investigations

The contact angle is a good indicator of the state of wettability of sample surfaces. An equal volume of distilled water was placed on every sample by means of a micropipette, forming a drop or spreading on the surface. After depositing HA, the corresponding surfaces had remarkably reduced contact angles. The sample S1 present a hydrophobic behaviour while sample S2 and S3 has a hydrophilic one.

The hidrophilicity is in a direct relation with the biocompatibility; the smallest contact angle the better biocompatibility.

The values obtained for every sample are summarized in Table 2.

Table 2. Contact angle for samples S1-S3

Sample	Contact angle (degree)
S1	93.24
S2	70.61
S3	56.05

3.4 ICP-MS determination

ICP-MS were performed in NaCl 9%. Samples S1-S3 were immersed in this solution for 24 hours. From ICP-MS data (figure 6) we can observe that after 14 and 21 days of immersion of CoCr alloy in SBF, the quantity of Co^{2+} and Cr^{2+} ions measured after 24 hours of immersion in NaCl 9% decrease compared with the same sample after one day of immersion in NaCl 9%, fact that put in evidence that the hydroxyapatite is stable and is a protective layer against corrosion in human body.

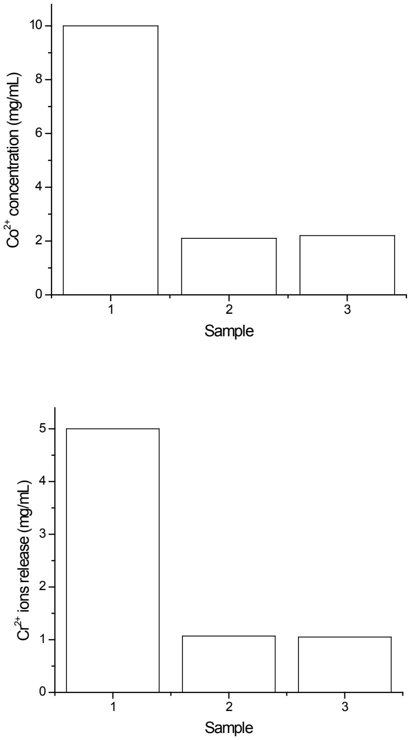

Figure 6. Co^{2+} (top) and Cr^{2+} (bottom) concentrations for samples S1-S3

4. Conclusions

The increase of immersion time of CoCr alloys in SBF lead to a more stable coating. After immersion in SBF after 14 days we obtained a precursor of hydroxyapatite and after 21 days of immersion in SBF we obtained hydroxyapatite with very good results. More investigations are needed to better control the composition of hydroxyapatite precursors deposited on CoCr alloys in order to use them for a particular application in the human body.

Acknowledgements

This work was supported by Romanian Ministry of Education and Scientific Research, as well as by Executive Agency for Higher Education, Research, Development and Innovation Funding, under projects PCCA 2- nr. 66/2014 and PCCA 2-nr. 166/2012.

References

1) A. Chiba, K. Kumagai, N. Nomura, S. Miyakawa, *Acta Mater.* 55 (2007) 1309.
2) N.G. Sotereanos, C.A. Engh, A.H. Glassman, G.E. Macalino, C.A. Engh Jr., *Clin. Orthop. Relat. Res.* 313 (1995) 146.
3) Carl Lindahl, Wei Xiaa, Håkan Engqvist, Anders Snis, Jukka Lausmaa, Anders Palmquist, *Applied Surface Science* 353 (2015) 40.
4) F.H. Lin, Y.S. Hsu, S.H. Lin, J.S. Sun, *Biomaterials* 23 (2002) 4029.
5) X. Liu, P. Chu, C.X. Ding, *Mater. Sci. Eng. Rep.* 47 (2004) 49.
6) L.L. Hench, *J. Am. Ceram. Soc.* 74 (1991) 1487.
7).R.H. Doremus, *J. Mater. Sci.* 27 (1992) 285.
8) T.J. Webster, E.A. Massa-Schlueter, J.L. Smith and E.B. Slamovich, *Biomaterials* 25 (2004) 2111.
9) T.J. Webster, C. Ergun, R.H. Doremus, R.W. Siegel and R. Bizios, *Biomaterials* 21 (2000) 1803.
10) F.Barrčre, CM van der Valk, R.A.J Dalmeijer, G. Meijer, CA van Blitterswijk, K de Groot, P.Layrolle, *J. Biomed. Mater. Res. A* 66 (2003) , 779.
11) F.Barrčre, CM van der Valk, R.A.J Dalmeijer, K de Groot, P.Layrolle, *J.Biomed. Mater. Res. B* 67 (2003) 655.
12) E Aldea, N. Badea, I Demetrescu, *Rev. Chimie* 58, (9) (2007) 918.
13) E. Boanini, P. Torricelli, M. Gazzano, *Biomaterials* 27 (2006) 4428.
14) J. Forsgren, F. Svahn, *Acta Biomaterialia* 3 (2007) 980.
15) H. Najafi, Z.A. Nemati, Z. Sadeghian, *Ceram. Int.* 35 (2009) 2987.
16) C. Kaya, I. Singh, A.R. Boccaccini, *Adv. Eng. Mater.* 10 (2008) 131.
17) Q. Chena, H. Liua, Y. Xinb, X. Chenga, *Electrochim. Acta* 111 (2013) 284.