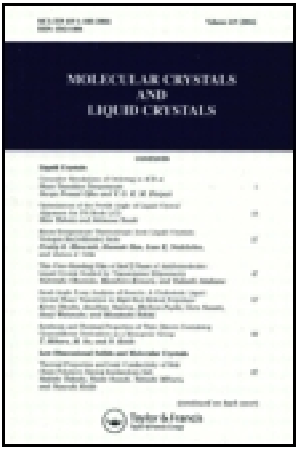

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M. M. Sovar [a] , I. Man [a] & I. Demetrescu [a]
[a] Faculty of Applied Chemistry and Material Science, University Politehnica of Bucharest, Bucharest, Romania

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Enhancing Corrosion Resistance of CoCr Alloy using Bioactive Phosphate Deposition

M. M. Sovar, I. Man, and I. Demetrescu
Faculty of Applied Chemistry and Material Science, University
Politehnica of Bucharest, Bucharest, Romania

The present study focused on the connection between biocompatibility and corrosion resistance for a CoCr alloy. The behavior of a CoCr biomaterial was studied by electrochemical (cyclic voltametry), Fourier transform infra-red spectroscopy (FTIR), surface analysis techniques as scanning electronic microscope (SEM) and X-ray diffractometer (XRD). The surface analysis confirms electrochemical data and the effect of bioactive film on stability.

Keywords: biocompatibility; chemical phosphate deposition; CoCr alloy; electrochemical behaviour; surface analysis

INTRODUCTION

CoCr alloy was used in the fabrication of prostheses since 1940, and the integrity of his passive film and the ion release was intensively discussed taking into account that local breakdown or tribocorrosion process lead to dissolution of metal ions in the body. The modern CoCr alloy used as biomaterial is the one with a composition according ASTM F-75 [1]. This paper is focused on improving the corrosion resistance and integration capacity of a CoCr implant alloy, with a composition close to ASTM F-75, but nickel free. This investigation is based on idea that a bioactive thin film of calcium-phosphate is a way to enhance film quality.

The use of CoCr alloys for surgical applications is mainly of interest for orthopedic prostheses for knee, shoulder and hip. For long-term requirements in arthroplasty, a high corrosion resistance combined

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Address correspondence to Meria Magdalena Sover, University Politehnica of Bucharest, Faculty of Applied Chemistry and Material Science, Str.Polizu, Nr. 1,011061, Bucharest, Romania. E-mail: ela_magda@yahoo.com

with a good biocompatibility is needed. The fabrication process with the use of Co, Cr and Mo allows achieving extremely hard implants with a high corrosion resistance in body fluids [2].

Various surface treatments like mechanical treatment, electrochemical treatment (anodizing), heating, plasma coatings, calcium phosphate coatings have been all studied to achieve desired surface properties on CoCrMo alloys [3,4].

Phosphate deposition is a way to decrease ion release from CoCr alloy and also to increase the biocompatibility of the alloy, obtaining a good combination between corrosion resistance and biocompatibility of the surface.

A chemical treatment followed by a biomimetic deposition of Ca/P allows the deposition of apatite layer on the surface of the implant. This method is one of the used methods to improve the bioactivity of materials, and shows the following advantages in comparison with the traditional methods [6]: 1) it is a low temperature process that can be applied to any temperature sensitive substrate, 2) it forms apatite crystals, similar to those of bone, showing good bioactivity and good resorption characteristics, 3) it can be deposited even in porous substrates or implants of complex geometries, 4) it can incorporate bone growth features [5,6].

Electrochemical coating [7] is a convenient procedure, but the deposition proposed by immersion in simulated body fluid (SBF), after a chemical treatment [8] in 5 M NaOH for 10 hours, is simpler and the stability and integration capacity of the film is improving. It was shown that alkaline treatment improves the surface of metals from corrosion attack and 5 M NaOH treatment shows a maximum efficiency towards corrosion resistance and could act as an effective method for further treatments.

In the present investigation an attempt has been made to study the effect of alkali, sodium hydroxide on a CoCr alloy followed by a biomimetic deposition from a SBF solution of HAP coatings on this chemically treated surface, towards corrosion resistance. The conditions were optimized. The sample was evaluated electrochemically through cyclic polarization experiments performed in Hanks solution. The results obtained were compared with that of untreated alloy. Other analysis methods were used in order to see the structure of the formed layer.

EXPERIMENTAL DETAILS

The chemical composition of the alloy is: Co 61.93%; Cr 27.45%; Mo 6,19%; Fe 1,46%; O 0,54% and the testing solution was solution Hank with following composition: NaCl 8 g/L, $NaHCO_3$ 0.350 g/L, KCl

0.4 g/L, $NaH_2PO_4{}^*H_2O$ 0.25 g/L, $Na_2HPO_4{}^*2H_2O$ 0.06 g/L $MgCl_2$ 0.19 g/L, $CaCl_2{}^*2H_2O$ 0.19 g/L, $MgSO_4{}^*7H_2O$ 0.06 g/L, 1 g/L glucose and pH = 6.9.

The sample was abraded with SiC sand paper 600–4000, degreased in benzene for 5 minutes and prolonged rinsed with distilled water and after dried in hot air.

In the chemical treatment the CoCr alloy was soaked in 5M NaOH solution at 60°C for 10 h. The alkali treated samples were washed in deionizer water and dried at 100°C for 30 minutes. A calcium phosphate coating was produced on substrate by immersion in a solution that simulates body fluid – SBF, with following composition: NaCl 7.9344 g/L, $NaHCO_3$ 0.350 g/L, KCl 0.222 g/L, K_2HPO_4 0.174 g/L, $MgCl_2 \cdot 6H_2O$ 0.303 g/L, $CaCl_2 \cdot 6H_2O$ 0.545 g/L, $Na_2SO_4 \cdot 10H_2O$ 0.161 g/L, for 3 day and then in a solution 5 SBF (a solution with Ca^{2+} concentration 5 times higher) for other 3 days [9].

The coating properties were evaluated through electrochemical, spectral, morphological and structural properties according following technique: ***FTIR*** spectra using a Jasco 620 spectrophotometer, ***Ciclic voltamentry*** with a Voltalab 40 equipment and a Voltamaster soft, ***ESEM*** with Environmental Scanning Electron Microscope FEI Inspect ESEM, ***X-ray diffraction (XRD)*** measurements with a DRON UM1 diffractometer connected with PC, in Bragg–Brentano geometry. The used radiation was CuK_α, and in the diffracted fascicle was a graphite monocromator.

RESULTS AND DISCUSSION

Potentiodynamic Polarization Experiments

The length of the passive domain gave us information regarding the behaviour of the oxide film from the surface of the alloy; larger domain of the potential values indicates a more stable film. In our case the passive domain for the two analysed samples overlap on the potential values that are met frequently in the human body (−300–300 mV), but for the treated sample this domain is larger than that obtained for the untreated one.

The potentiodynamic polarization curves were obtained with a scan rate of 2 mV/s between −800 mV and +1200 mV. Platinum and Ag/AgCl electrodes served as an auxiliary electrode and a reference electrode respectively. The data statistical treatment was performed with a Medcalc program for biomedical application.

In Figure 1 the cyclic voltametry curves are presented for CoCr alloy untreated and chemical treated.

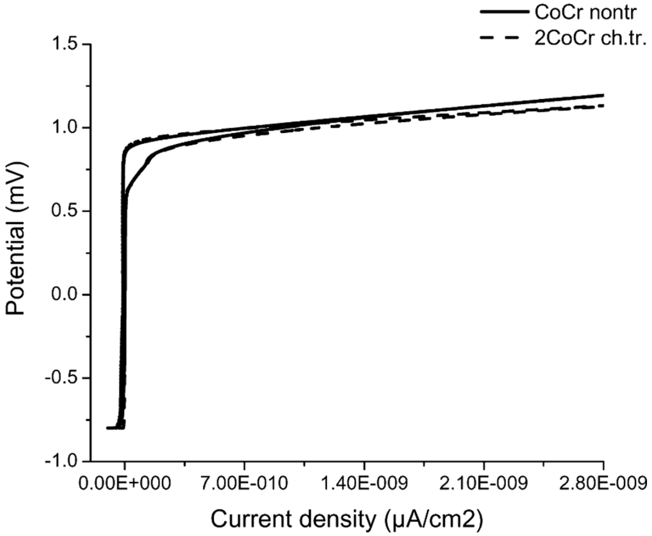

FIGURE 1 Potentiodynamic polarization curves of CoCr alloy in Hank solution.

A greater corrosion resistance of the treated sample could be seen also from the values of the corrosion rate, which is much smaller for the treated surface in comparison with the untreated one.

The values obtained from cyclic voltametry for corrosion potential (E_{cor}), current density (i_{cor}), corrosion rate (v_{cor}) and for the passive domain could be seen in the Table 1. The current density and corrosion rate decrease for the chemical deposition.

Fourier Transform Infra Red Spectroscopy (FTIR)1

The chemical coating induces hydroxyapatite formation (HA) sustained in FTIR spectrum (Fig. 2) by the presence of hydroxyl group at around 3427 cm^{-1}, carbonate group at around 874, 1423 and 1603 cm^{-1}, and phosphate group PO_4^{-3} at 1028 cm^{-1} and 602 or 561 cm^{-1} representing ν4 O–P–O bending vibration [7].

TABLE 1 Potentiodynamic Polarisation Data Sample in Hank Solution

Sample	E_{cor} (mV/SCE)	i_{cor} (μA/cm^2)	v_{cor} (mm/year)	Domain passive (mV)
CoCr nontr	−163	0.88	0.0089	1201
2CoCr ch · tr.	−131	0.09	0.0009	1337

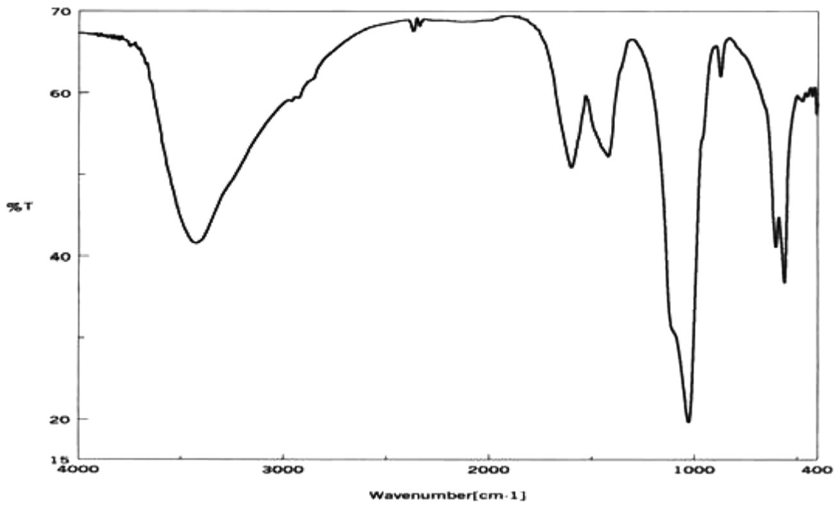

FIGURE 2 FTIR spectrum of HA coating.

Scanning Electron Microscopy (SEM)

From SEM analyses it was obtained the composition and the morphology of the chemically deposited film from the surface of the alloy.

Figure 3 shows SEM micrograph and spectrum for emission in X-ray of the chemically coating.

The surface is completely heterogeneous presenting a granular structure of the formed layer. Also the surface is not so well covered, this feature could be seen from the labels of the elements from the surface of the analysed surface of treated sample. This aspect probably could be improved by increasing the immersion time in SBF.

X-ray Diffraction (XRD)

X-ray Diffraction data sustain FTIR spectrum. The XRD of calcium phosphate films were collected at room temperature. Data acquisitions were made with a DRON UM1 diffractometer connected with PC. A horizontal powder goniometer in Bragg–Brentano focusing geometry with graphite monochromator was used. The incident $Cu-K_{\alpha}$ radiation, $\lambda = 1.54178\,\text{Å}$, at 45 kV and 30 mA was used. The typical experimental conditions were: 20 s for each step, range angle $2\theta = 25–35^{\circ}$, step 0.02°.

The patterns obtained in the conditions were used to identify the calcium phosphate crystalline phase. Two phases (Fig. 4) as followings

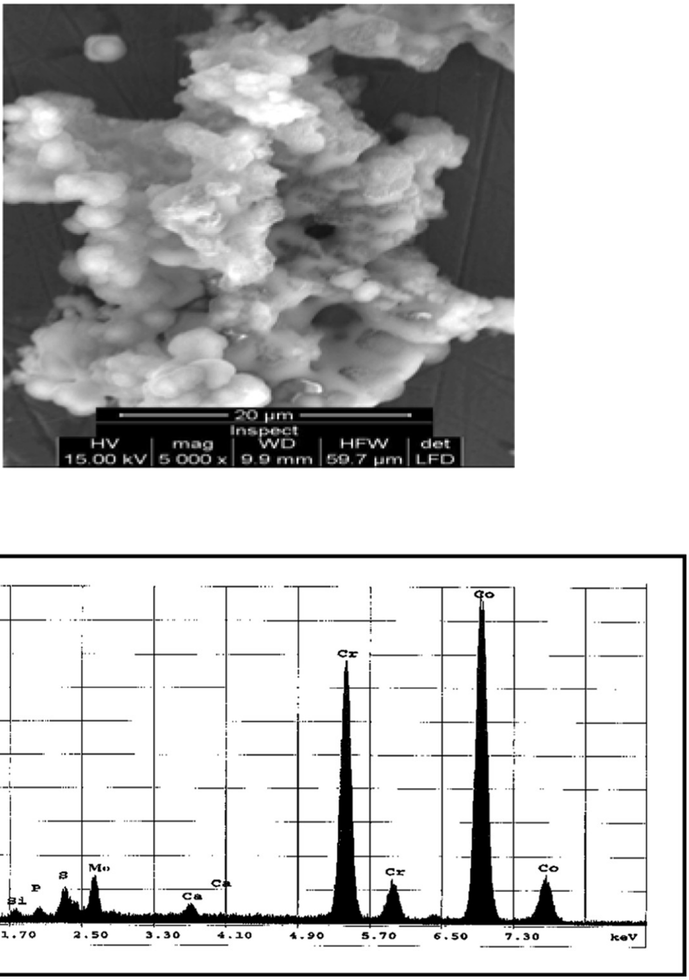

FIGURE 3 SEM image and spectrum for emission in X-ray of the chemically deposited Ca/P on the surface of CoCr alloy.

were observed: $Ca_5(PO_4)_3(OH)$ – the hexagonal crystalline system, the Pearson symbol hP46/3 and $Ca_9HPO_4(PO_4)_5OH_5OH$ – the hexagonal crystalline system. The peak from 26° indicate the fact that the film growth after the direction of the substrate and that has a monocrystaline behavior.

The diffraction peaks are very broad and the intensities are low. These can be explained by very small crystallite size and high strain in thin films.

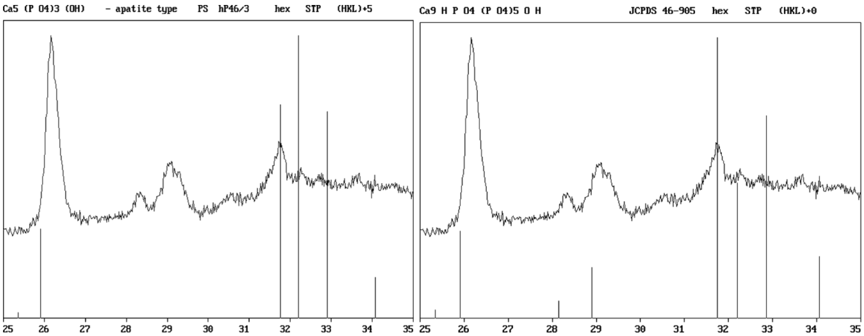

FIGURE 4 XRD patterns curves for CoCr alloy chemical treated.

CONCLUSIONS

The stability of the oxide film is supported by electrochemical investigation: cyclic polarization. The current density and corrosion rate decrease for the chemical deposition.

The infrared (FTIR) data confirmed HA formation having the existence of hydroxyl, carbonate and phosphate bands.

SEM, EDAX and X-ray analysis on chemical phosphate deposition permit selection of a suitable bioactivation of CoCr alloy. The X-ray diffraction was used to identify the calcium phosphate crystalline phase.

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