

ELECTRODEPOSITION AND CORROSION BEHAVIOR OF HYDROXYAPATITE ONTO TITANIUM

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Abstract

The present study includes the results of the hydroxyapatite electrochemical deposition on titanium substrate from 3 solutions of different concentrations of precursors. The deposited HA layers and the substrate were studied by means of x-ray diffraction and scanning electron microscopy, and also corrosion resistance tests have been performed. Results confirmed the formation of low crystallinity hydroxyapatite coatings, displaying fine layers of feathery crystals and other structures resulted from agglomeration phenomena. Corrosion tests, performed in artificial saliva solution, showed that the corrosion resistance of the hydroxyapatite coated Ti sample obtained from 0.875M Ca and 0.525M P precursors solutions was higher than that of the other samples.

Introduction

Hydroxyapatite (HA) - chemical formula $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ - alone or deposited onto metallic substrates, is highly used in the biomedical field, due to undeniable advantages such as: biocompatibility, bioactivity and osseointegration [1,2]. One of the drawbacks of hydroxyapatite is its low mechanical resistance. The deposition of hydroxyapatite onto metallic substrates, such as titanium, provides the means to ensure the mechanical resistance of any implant, besides the mentioned biochemical advantages. Several methods have been developed regarding the deposition of HA coatings on metal substrates, including the electrochemical deposition method, having several advantages [3] such as: homogeneity, availability of deposition onto complex shape substrates, possibility to control the layer thickness on demand, etc.

Considering its long-term presence in the body, any implant should possess certain characteristics, including high corrosion resistance - as is the case with metal-hydroxyapatite implants [4].

This study aims to prepare HA coatings on titanium substrates by electro-deposition from precursors solutions having three different concentrations, and compare their corrosion behaviour by potentiodynamic polarization test in artificial saliva solution.

Experimental

The electrolyte solutions used for the electrochemical deposition were prepared from separate solutions of analytical grade $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (Sigma Aldrich) and analytical grade $(\text{NH}_4)_2\text{HPO}_4$ (Merck) of different concentrations, as presented in Table 1.

Solutions were considered so as to preserve the Ca:P ratio of 10:6, as in natural hydroxyapatite. The pH level was kept in the 8.3-8.4 range, being adjusted with ammonia, after mixing the two precursor solutions.

Table 1. Details of the solutions concentrations used in the deposition process

Sample number	Ca and P precursors	
	Ca(NO ₃) ₂ ·2H ₂ O solution concentration (mM)	(NH ₄) ₂ HPO ₄ solution concentration (mM)
1	0.875	0.525
2	1.75	1.05
3	3.5	2.1

Before the electrochemical deposition, the Ti discs ($\phi = 1$ cm) were polished using SiC sandpaper of different grit sizes and felt, washed with acetone, placed in ethanol/acetone mixture 50:50 for 30 minutes in an ultrasonic bath, rinsed with bidistilled water and dried.

The electrochemical setup consisted in a PGZ 402 Voltalab potentiostat and a three-electrode glass cell with heating mantle. The working electrode was a titanium disc (used as the cathode), a platinum plate was used as counter electrode and the saturated calomel electrode (SCE) coupled to a salt-bridge junction was used as reference electrode. The electro-deposition took place at 80°C, at a constant potential of -1500 V, for 1h. After the deposition, the samples were dried at 40°C in an oven, and were investigated by x-ray diffraction (XRD), using a PANalytical X'Pert Pro MPD Diffractometer with Cu anode, working parameters 45 kV and 30 mA. Images of the samples surfaces were obtained using a Phillips Inspect S scanning electron microscope.

The Fusayama – Meyer simulated saliva solution (pH=5.8) of the following chemical composition [5]: NaCl (0.4 g/L); KCl (0.4 g/L); CaCl₂ (0.6 g/L); NaH₂PO₄·H₂O (0.79 g/L), urea (1 g/L) and Na₂S·9H₂O (0.005 g/L) was used as the testing electrolyte in corrosion studies at 37°C.

The electrochemical cell for corrosion tests included: a working electrode consisting in an uncoated or coated sample, a platinum wire as counter electrode and the SCE. Each sample was allowed to reach a steady open circuit potential (OCP) for 1h. Afterwards, a potentiodynamic polarization was initiated from -800 up to + 300 mV (vs. SCE), at a sweep rate of 1 mV/s.

Results and discussion

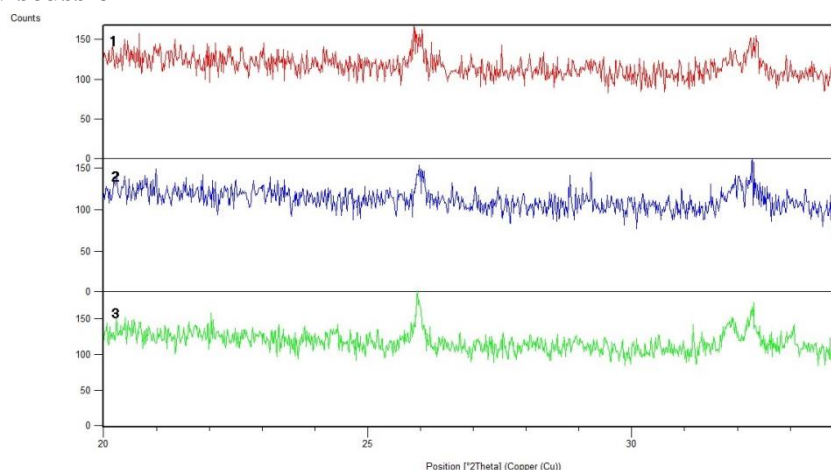


Figure 1. XRD patterns of the 3 deposited HA layers onto Ti, concentration order 1<2<3

The XRD results are presented in Figure 1, which confirm the hydroxyapatite formation, but with low crystallinity.

With increasing concentration (sample 3), the peaks resolution improves. The size of the peak at 25.96 2theta, representing the 002 crystallographic plane, is an indication of an elongated shape of the crystals.

Scanning electron microscopy (SEM) images are presented in Figure 2. For sample 1, with the smallest concentration used, the deposited layer is fairly uniform, with rare spherical arrangements of needle-shaped crystals. Increasing the concentration (sample 2) leads to extended areas of interconnected over-grown spherulites, while the substrate is covered with a uniform layer of feathery crystals. Increasing the concentration even more (sample 3) does not change the appearance of the deposition, but leads to an agglomeration of the crystals in the over-grown regions. In all cases the crystals are submicrometric in size, and all the substrates are covered with a fine layer of feathery crystals.

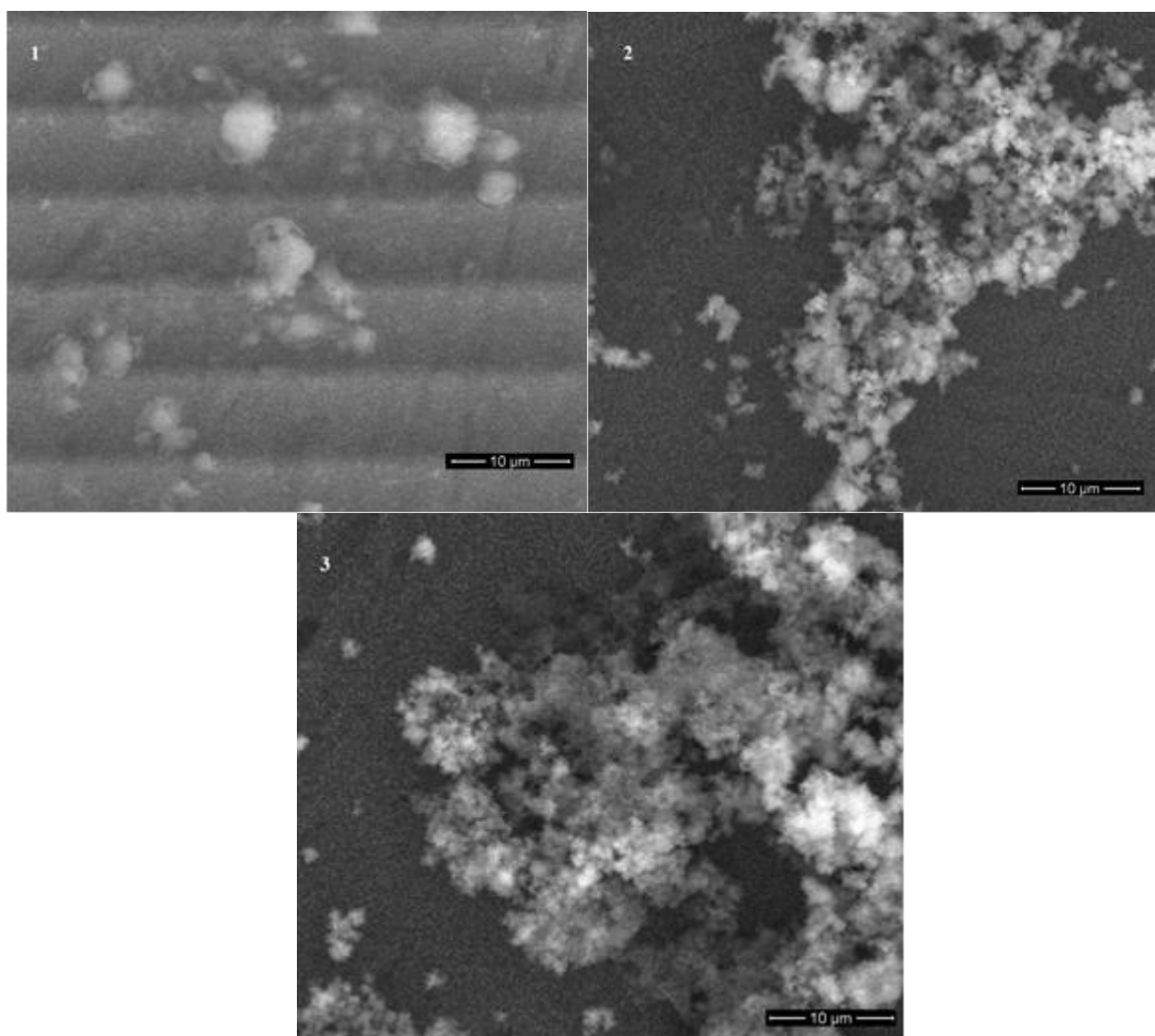


Figure 2. SEM images of the 3 deposited layers of HA onto Ti, concentration order $1 < 2 < 3$. The agglomeration increases in the order $1 < 2 < 3$ and is due to: on one side, the increase of concentration, and on the other side, to the alkaline pH where the deposition took place, favouring the existence of a large amount of available OH. All these findings indicate an accelerated nucleation and, as a consequence, a big number of small crystals and low growth rate.

The potentiodynamic polarization curves of the Ti samples, uncoated and coated with HA, in artificial saliva solution, at 37 °C, are shown in Figure 3.

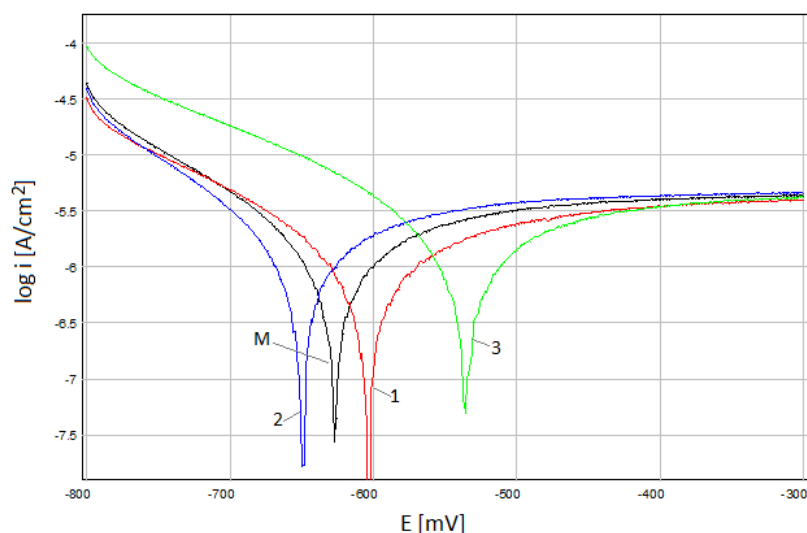


Figure 3. Potentiodynamic polarization curves for uncoated Ti (M) and coated with three different HA layers (1÷3).

Corrosion potential (E_{corr}) and corrosion current density (i_{corr}) determined by the Tafel extrapolation method and corrosion rate (v_{corr}) for each sample are shown in Table 2.

Table 2. Electrochemical parameters obtained from the Tafel extrapolation plots.

Sample	E_{corr} [mV]	i_{corr} [$\mu\text{A}/\text{cm}^2$]	v_{corr} [$\mu\text{m}/\text{year}$]
M	-628	1.17	10.20
1	-605	0.90	7.82
2	-651	1.30	11.28
3	-536	1.53	13.31

Sample 1 presents a lower value ($0.90 \mu\text{A}/\text{cm}^2$) for the i_{corr} parameter by comparison with both HA coated samples (2 and 3) and uncoated Ti discs (M). Also, the E_{corr} value is more electropositive than that of uncoated Ti, indicating that the corrosion resistance of Ti is improved by this HA coating.

Regarding *Sample 3* a different behaviour can be noticed, namely: it shows the most electropositive E_{corr} value (-536 mV), but the i_{corr} value is a little higher than the one obtained for uncoated Ti, indicating that the HA coating provides poor corrosion protection for Ti metal. The same conclusion can be drawn for *sample 2*, where the i_{corr} value was also higher than the one for uncoated specimen. The E_{corr} values are in good agreement with the values obtained from OCP measurements (not presented here).

Therefore, the corrosion behaviour of the HA coating obtained using the smallest concentrations of precursors from this study revealed a slower corrosion rate for Ti substrates ($7.82 \mu\text{m}/\text{year}$) than the other coatings (which act as corrosion activators).

These results indicate that the presence of the HA deposited from diluted electrolyte solution (the most uniform layer) can reduce the corrosion rate of Ti by acting as a barrier to the transport of ions and electrons between the substrate and the electrolyte, thus reducing the electrochemical reaction rate [6].

Conclusions

HA coatings were successfully formed on Ti substrate by electrochemical deposition, as confirmed by XRD studies. SEM micrographs revealed that all the substrates were covered

with a fine layer of feathery crystals and as the concentrations of the precursors increased, other structures were formed as a result of agglomeration phenomena.

The corrosion rate determined from polarization curves was high for samples 2 and 3, but for sample 1 it was lower than the other samples, including the uncoated Ti substrate. Thus, the electrochemical test, performed in artificial saliva solution, showed that the corrosion resistance of the HA coated Ti sample obtained from 0.875M Ca and 0.525M P precursors was higher than that of the bare Ti electrode.

Based on these results, it might be concluded that some HA coatings can moderately decrease the corrosion rate of Ti substrates in physiological environment, while others can accelerate it. Based on the SEM data, it seems that in the absence of significant agglomeration phenomena, the HA coating provides better corrosion protection.

The electrochemical synthesis parameters, in particular the concentration of the electrolyte, affect the crystallinity, morphology and corrosion protection of the resulting coatings.

References

- [1] A. I. Bucur, R. Bucur, T. Vlase, and N. Doca, "Thermal analysis and high-temperature X-ray diffraction of nano-tricalcium phosphate crystallization," *J. Therm. Anal. Calorim.*, vol. 107, no. 1, pp. 249–255, 2012.
- [2] A. I. Bucur, R. A. Bucur, Z. Szabadai, C. Mosoarca, and P. A. Linul, "Influence of small concentration addition of tartaric acid on the 220 °C hydrothermal synthesis of hydroxyapatite," *Mater. Charact.*, vol. 132, pp. 76–82, 2017.
- [3] D. T. M. Thanh *et al.*, "Controlling the electrodeposition, morphology and structure of hydroxyapatite coating on 316L stainless steel," *Mater. Sci. Eng. C*, vol. 33, no. 4, pp. 2037–2045, 2013.
- [4] B. Singh, Gurpreet; Singh, Hazoor; Singh Sidhu, "Characterisation and In Vitro Corrosion Resistance of Plasma-Sprayed Hydroxyapatite and Hydroxyapatite – Silicon Oxide Coatings on 316L SS," *Bull. Mater. Sci.*, vol. 37, no. 6, pp. 1519–1528, 2014.
- [5] J. Qiu, W. Q. Yu, F. Q. Ohang, R. J. Smales, Y. L. Ohang, and C. H. Lu, "Corrosion behaviour and surface analysis of a Co-Cr and two Ni-Cr dental alloys before and after simulated porcelain firing," *Eur. J. Oral Sci.*, vol. 119, no. 1, pp. 93–101, 2011.
- [6] Z. Chun-Yan, Z. Rong-Chang, L. Cheng-Long, and G. Jia-Cheng, "Comparison of calcium phosphate coatings on Mg-Al and Mg-Ca alloys and their corrosion behavior in Hank's solution," *Surf. Coatings Technol.*, vol. 204, no. 21–22, pp. 3636–3640, 2010.