U.P.B. Sci. Bull., Series B, Vol. 71, Iss. 4, 2009 ISSN 1454-2331

EFFECT OF HYDROXYAPATITE ON INTERFACE PROPERTIES FOR ALLOY/BIOFLUID

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Lucrarea se referă la proprietățile de suprafață ale titanului şi aliajelor sale (TiAlZr, TiAlVMoFe), acoperite şi neacoperite cu hidroxiapatită (HA). Acoperirile de HA au fost obținute electrochimic prin metoda potențiostatică în soluții apoase de 0.61mM Ca(NO3)2 şi 0.36mM NH4H2PO4. Evaluarea proprietăților de la interfață s-a efectuat folosind microscopia electronică de baleiaj (SEM), măsurători de unghi de contact (CA), polarizare ciclică, teste de stabilitate a HA. Acoperirea cu HA a dus la schimbarea caracterului suprafeței titanului şi a aliajelor sale de la hidrofil la puternic hidrofil şi la îmbunătățirea rezistenței la coroziune a titanului şi a aliajelor sale.

This paper is focused on surface properties of titanium and titanium alloys (TiAlZr, TiAlVMoFe) covered and uncovered with hydroxyapatite (HA). The coatings were obtained electrochemical using the potentiostatic method in aqueous solutions of 0.61mM Ca(NO3)2 and 0.36mM NH4H2PO4. Interface properties evaluation was perform using scanning electron microscopy (SEM), contact angle measurements (CA), cyclical polarization and HA stability tests. The covering with HA leads to changes in the character of titanium and titanium alloys surfaces character from low hydrophilic to strong hydrophilic and improve the titanium and titanium alloys corrosion resistance.

Keywords: hydroxyapatite, contact angle, titanium alloys, electrochemical measurements

1. Introduction

Hydroxyapatite (HA) [1] is widely used as bioceramics in reconstructive surgery, in dentistry and as drug delivery materials due to the good biocompatibility and osteoconductivity [2]. One of the limitations for the usage of these materials is their low mechanical strength. Combining the biocompatibility and bioactivity of HA with the high strength and toughness of metals could be a good idea for loaded-bearing applications in orthopedic and dental surgery. Many

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different techniques have been used for the preparation of HA coatings. Among them are ion sputtering, plasma spray, sol–gel, electrochemical deposition and a biomimetic processes. The electrochemical deposition is one of the most promising new processes. The advantages of electrochemical deposition include good control of composition and structure of the coatings, relatively low processing temperatures that enable formation of highly crystalline deposits with low residual stresses, and the ability to deposit on non-line-of-site, porous or complex surfaces [3,4].

The structure of the coating can be controlled by changing the composition, pH, temperature of the electrolyte, and also by the applied potential and current density.

The aim of the paper is to compare the surface properties of titanium [5] and titanium alloys (TiAlZr, TiAlVMoFe) covered and uncovered with hydroxyapatite (HA).

2. Experimental part

2.1. *Preparation of samples*

In this study were used Ti alloys plates prepared by R&D, Consulting and Services, Bucharest, Romania, by vacuum melting (size: 10×10×1mm) [6,7].

Samples were abraded using a SiC sandpaper no 800 then were rinsed using a mixture of hydrofluoric and nitric acid (HF/HNO_3) at a ratio of 1:3 and finally they were washed with acetone and distilled water. The composition of studied samples in weigh percent is presented in the Table 1.

Table 1

Composition of the studied alloys

Sample	Ti	Mo	V	Al	Zr	Fe
Ti	~ 99.2	-	-	0.05	-	0.095
TiAlVMoFe	86	1.95	2.87	6.93	-	2.20
TiAlZr	87	-	4.5	6.75	1.25	-

2.2. *Electrochemical deposition*

Electrodeposition was carried out in a standard three-electrode cell, where a platinum foil was used as the auxiliary (counter) electrode and a saturated Ag/AgCl electrode as the reference electrode. The electrolyte was prepared by dissolving 0.61mM $Ca(NO_3)_2$ and 0.36mM $NH_4H_2PO_4$ in Millipore water. A Voltalab equipment potentiostat/galvanostat operating in potentiostatic mode was employed to maintain the cathode potential at -1.4V vs. Ag/AgCl for 2 h. The environment temperature was controlled at 85^0C.

2.3. *Spectroscopic analysis and morphology characterization of calcium phosphate based coatings*

The aspect, morphology surface, structural and elemental analysis of electrodeposited coating, composition of protective films formed on the metallic surfaces [8,9,10] were studied by scanning electron microscopy (SEM) coupled with EDS (energy dispersive spectrometry) using Environmental Scanning Electron Microscope FEI/Phillips XL 30 ESEM at a pressure = 0.7 Torr working way GSE (water vapours).

2.4. *Potentiodynamic polarisation studies*

Potentiodynamic polarisation studies were carried out at the initial time t_o=0h of immersion in simulated body fluid (SBF) for titanium alloys. All the potential measurements were carried out with a reference electrode of Ag/AgCl. The counter electrode employed for the potentiodynamic polarisation studies was platinum foil and the potentials were scanned at a rate of 2 mV/s in an aerated medium. A Voltalab Potentiostat with VoltaMaster program was used to conduct the polarisation experiments. In order to obtain reliable results, polarisation experiments were triplicated in SBF solution. The composition of SBF was: 142 mM Na^+, 5mM K^+, 2.5 mM Ca^{2+}, 1.5mM Mg^{2+}, 147.8 mM Cl^-, 4.2mM HPO_4^{2-}, 0.5 mM SO_4^{2+}.

2.5. *Determination of Ca^{2+} ion content in bioliquids*

An ICP-MS, ELAN DRC-e Perkin Elmer SCIEX U.S.A. was used for Ca^{2+} determinations. The detection limit was 0.001 $\mu g.g^{-1}$. The covered titanium alloys plates were introduced in SBF for different periods of time and the solutions were analyzed. Samples were introduced with an *in-situ* nebulizer/vapor generator sample introduction system. The conditions were selected in order to maximize the calcium ion signal while a solution containing 5 $ng.mL^{-1}$ of Ca^{2+} was introduced into the vapor generating system. The generated vapor was then transported to the ICP-MS for calcium determination.

2.6. *Wettability tests*

Contact angle measurements were carried out with 100 Optical Contact Angle Meter - CAM 100 in order to evaluate the wettability of the surface-modified alloy as a result from each treatment. An equal volume of distilled water was placed on every sample by means of a micropipette, forming a drop or spreading on the surface.

3. Results and discussion

3.1. *Electrolytic deposition*

Fig. 1 shows the typical current density transients monitored during potentiostatic deposition of HA on titanium and its alloys.

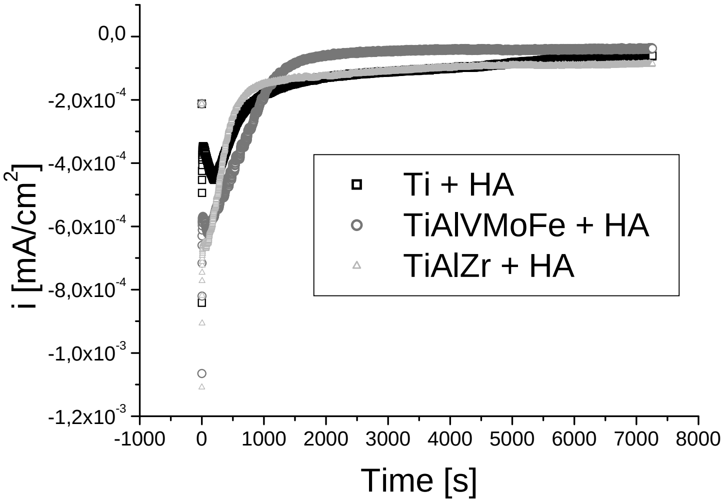
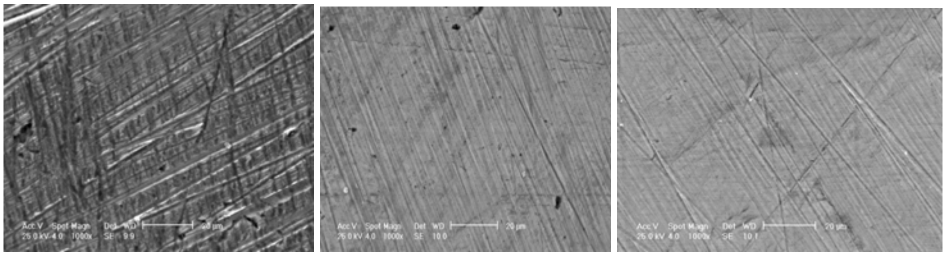


Fig. 1 Current densities for Ti and Ti alloys in time.

The transient for HA on titanium and its alloys is similar to that reported and analyzed by Eliaz et al. [11]. The transients may be divided into three periods. First, the charging of the double layer leads to a rapid current decay. Next, the current starts to increase in anodic direction due either to the growth of independent nuclei or to the growth of dependent nuclei and simultaneous increase in number of nuclei. During the third period, a one-dimensional diffusion limit is introduced by an overlap between the diffusion fields around growing nuclei, while growth of independent nuclei continues. Consequently, the nucleation rate decreases gradually until, eventually, the growth centers contact one another and the growth stops.

3.2. *Spectroscopic analysis and morphology characterization*

Fig. 2 presents the SEM image of the Ti, TiAlZr, TiAlVMoFe electrode surfaces. Using SEM with EDS (energy dispersive spectrometry) analysis, it can be observed that on the surface of the electrodes appears a passive layer composed by TiO_2 and small quantities of other oxides that forms the titanium alloys. Also, the surface has different roughnesses.



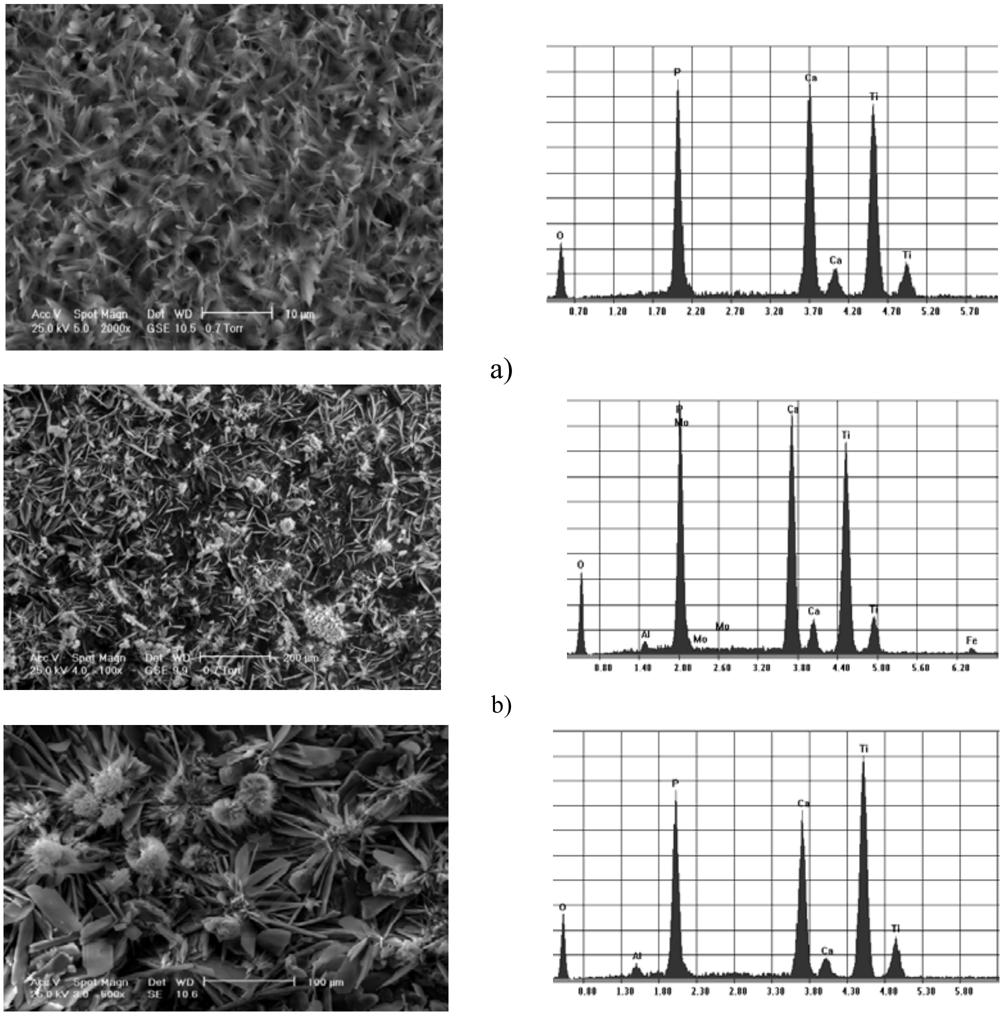
Ti TiAlMoFe TiAlZr

Fig .2 The SEM image of the Ti, TiAlZr, TiAlVMoFe.

Fig. 3 shows the SEM image for TiAlVMoFe, TiAlZr and the EDS spectrum after electrodeposition. It is observed that some systems appear like a booklet with unique morphology and constant thickness. The thickness of the layer is relatively small because according to the X-ray emission spectrum. (obtained by EDS and presented in Fig. 3a, a titanium peak appear besides the ones for Ca, P and O). The presence of Ca, P and O puts in evidence the formation of some precursors of HA. Fig. 3b presents the growth start of Ca/P coating on the TiAlVMoFe support in the initial stage; it presents a structure of dandelion bud that continues to increase like an inflorescence.

In Fig. 3c is presented the calcium phosphate based coatings deposition on the TiAlZr alloy which increases as an inflorescence and later it develops like a booklet.

The EDS spectrum shows that the Ca/P ratio obtained on the surface of the electrodes was varied from one to another electrode. For the Ti electrode the Ca/P ratio was 1.62, almost the same value as the one for hydroxyapatite (1.67). On the TiAlVMoFe electrode, the Ca/P ratio obtained by EDS was 1,33, a specific value for octacalciumphosphate ($Ca_8(HPO_4)_2(PO_4)_4\ 5H_2O$-OCP) which is a precursor of hydroxyapatite in bones and teeth, with an important role in bones mineralization. The EDS spectrum on covered TiAlZr electrode shows that tricalciumphosphate (TCP) was formed by electrodeposition when the Ca/P ratio was 1.5.



a)

b)

c)

Fig. 3 SEM images for a) Ti, b)TiAlVMoFe, c) TiAlZr and the EDS spectra after each HA electrodeposition.

3.3. Potentiodynamic polarisation studies

Fig. 4 shows the cyclic polarization curves for uncover Ti and its alloys in simulated body solution, and fig 5 shows the cyclic polarization curves for covered samples.

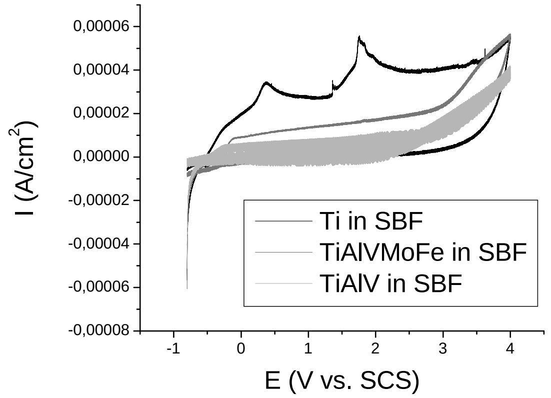


Fig. 4 Cyclic polarization curves for uncover Ti and its alloys in simulated body solution.

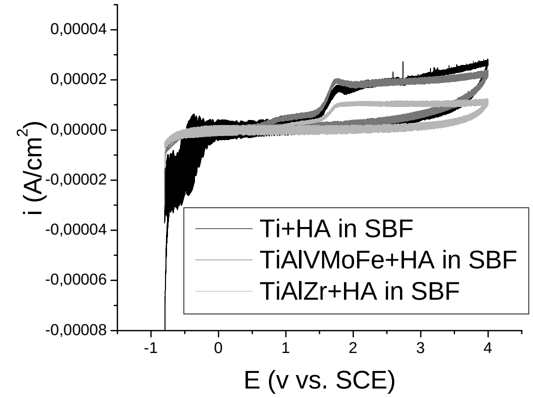


Fig 5 Cyclic polarization curves for covered samples.

The electrochemical parameters obtained by cyclic voltammetry are presented in the Table 2.

Table 2

Electrochemical parameters for covered and uncovered Ti and Ti alloys

Sample	E_{cor} (mV)	I_{cor} ($\mu A/cm^2$)	V_{cor} ($\mu m/y$)
Ti in SBF	-525.3	2.10	24.62
Ti+HA in SBF	-117.8	0.70	0.68
TiAlVMoFe in SBF	-341.9	1.01	11.85
TiAlVMoFe+OCP in SBF	-177.0	0.10	0.67
TiAlZr in SBF	-464.3	1.44	16.88
TiAlZr+TCP in SBF	-291.8	0.20	0.22

Where E_{cor}= the corrosion potential;

I_{cor}=the corrosion current;
V_{cor} = the corrosion rate.

The covered samples show another behaviour than the uncovered samples:

- the corrosion potential of the covered samples is more electropositive than the one for the uncovered samples;
- the corrosion currents for the covered samples are smaller than the one for uncovered samples;
- the corrosion rates are smaller for the covered samples than for uncovered samples.
- the efficiency of covering (e) is $e_{TiAlZr}>e_{Ti}>e_{TiAlVMoFe}$, the values being, respectively: 98.69>97.23>94.34.

The efficiency of covering is calculated with formula:

$$e = (Vcor\ without\ HA - Vcor\ with\ HA) / Vcor\ without\ HA$$

3.4. *Rate of coatings dissolution*

Fig. 6 presents the Ca^{2+} ions variation for Ti electrode covered with HA and the TiAlZr electrode covered with TCP. The dissolution rate of TCP is higher that the dissolution rate of HA. The solubility is greater for TCP than for HA. HA is the most stable coating under physiological conditions [2,12].

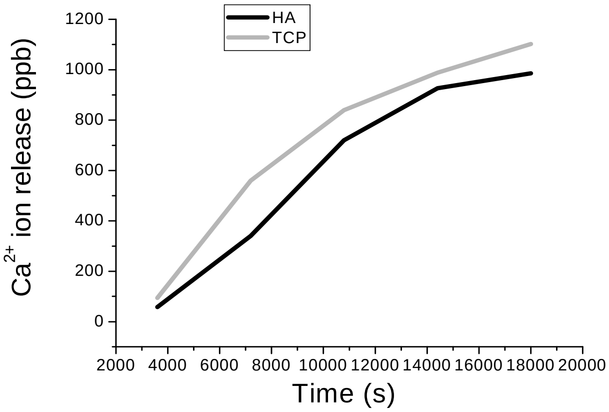


Fig. 6 Ca^{2+} ions variation for Ti electrode covered with HA and the TiAlZr electrode covered with TCP.

3.5. *Wettability tests*

Table 3 presents the values for the contact angle of the covered and uncovered samples. The presence of the covered layer leads to an decrease in the contact angle value and a increase of the hydrophilic behavior [13]. It has already been reported that low contact angles (below 30°) are promising for a successful osteointegration.

The contact angle for TiAlZr covered with TCP is smaller than for any other samples.

Table 3

Contact angle measurenment for covered and uncovered Ti and Ti alloys

Sample	Ti	Ti+HA	TiAlVMoFe	TiAlVMoFe+OCP	TiAlZr	TiAlZr+TCP
Contact angle	83.77	34.51	74.42	36.02	87.28	32.87

4. Conclusions

The electrochemical deposition method was used with good results to obtain calcium phosphate based coatings on titanium and titanium alloys surfaces.

In all the three cases, using different materials, it was observed the growth of the calcium phosphate based coatings on the surface of the samples. The presence of the coatings leads to a better electrochemical stability of materials. Also, the presence of calcium phosphate based coatings makes the surface more hydrophilic which improves the cell adhesion. The highest homogenity is present in the first case, at the Ti sample. In the other two cases, is initiated the growth of HA on the titanium alloys supports (TiAlVMoFe, TiAlZr), as some inflorescences that cover the entire surface and later become booklet like.

Considering that the titanium and titanium alloys studied in this paper are known implant biomaterials [14-16], their *in vitro* monitoring of HA deposition is useful for the understanding of the interface.

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