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CORROSION AND BIOACTIVITY OF A BIOINSPIRED COATING ON TiZr ALLOYS

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This paper is focused on corrosion and bioactivity of coated Ti50%Zr alloy with hydroxyapatite-chitosan composite with a ratio 1:2. The morphology of the coating was investigated via SEM analysis. The electrochemical stability of coated Ti50%Zr was studied performing Tafel plots in SBF solution after various days of immersion. Based on electrochemical experimental data, immersing the coating for 28 days has led to the stabilization and bioactivation of the sample.

Keywords: hydroxyapatite, composite, SEM, electrochemical stability, bioactivation

1. Introduction

Titanium, zirconium and their alloys are important biomaterials used to restore, repair and regenerate bone tissue for both orthopaedic and dental applications [1-3]. The use of medical implants has expended during the pasts decades owing to increased life expectancy and improved implant technology. Developing affordable and improved lifelong biomaterials and manufacturing technology remains a challenge for materials engineers. In the last years, a variety of surface treatments was applied on implant materials. There are many kinds of surface modification such as: hydrothermal treatment [4], ion implantation [5], anodic oxidation [6], acid-etching [7], alkali and heat treatment [8], plasma spraying [9], laser deposition [10], electrophoretic deposition [11], electrochemical deposition [12] and sol gel preparation [13].

It is recognized that HA coatings favor prosthesis adhesion and also improve long term stability. However, HA particulate can migrate from the implanted site causing damage to healthy tissue. [14] To resolve this clinical problem, composite coatings based on HA and natural [15] or synthetic [16] polymers have been developed.

Incorporation of HA with chitosan, could improve the bioactivity and the bone bonding ability of the HA/chitosan composites. [17] The most effective method of bioactivity assession certainly relies on *in vivo* tests. However, such

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tests put the patients in potential unnecessary risks and raise ethical problems when animal models are involved. *In vitro* methods performed in an controlled laboratory environment, are most commonly used to assess the bioactivity of new materials by simulating specific biological phenomena. However *in vitro* tests are not able to reproduce the complexity of living organisms and hence they remain preliminary trials. The accepted method of testing biomaterials is to perform *in vivo* tests only after extensive tests *in vitro*. A relatively easy approach to test materials *in vitro* consists in soaking them in a simulated body fluid such as SBF [18]. SBF is an acellular liquid that has in the composition the same ionic elements of human plasma. These tests are carried out by soaking the sample into a fixed volume of SBF for a specified period under controlled conditions. The purpose of these tests is to verify if the biomaterial is able to develop HCA on its surface. The significance of SBF tests is still under debate due to their intrinsic limits, such as the inability to verify antibodies reactions [19].

In this study, the preparation of hydroxyapatite/chitosan (Hap/Cs) coating on TiZr alloys using an electrochemical depesosition method is attempted. After that the Hap/Cs coating was supposed of bioactivation test for various period of time. Finally was characterized the surface structure and stability of Hap/CA coating before and after soaking it in SBF.

2. Experimental part

2.1. Materials and solutions

2.1.1. Substrate pretreatment

The samples were polished with SiC paper grit 800, 1200 and 2400 and cleaned by ultrasonication in ethanol for 5 minutes. Then they were washed with distilled water. Prior to electrodeposition, the Ti50%Zr substrates were etched in 12M HCl at $80^{O}C$ for 1h, dried at room temperature and finally the electrodeposition of the coatings took place.

2.1.2. Electrodeposition process

The electrodeposition of HAp/CS coating onto etched Ti50%Zr substrates was carried out in a typical three electrode electrochemical cell. A Pt foil was used as counter electrode, a Ag/AgCl as reference electrode and the etched Ti50%Zr as working electrode. The electrolyte solution was a mixture of HAp solution (0.167 mol/L $CaCl_2$ and 0.1 mol/L $NH_4H_2PO_4$) and chitosan solution (0.5 g/L chitosan in acetic acid 1%). All the materials were provided by the Sigma Aldrich. The pH of HAp solution was adjusted to 6 by slowly adding NaOH. The electrodeposition parameters were set according to a protocol described in a previous paper [20]. The electrodeposition process took place at -1500 mV for 90 minutes at $80^{O}C$.

The coating process of Ti50%Zr was performed with a component ratio of HAp:CS= 1:2, which according to previous papers is the most stable one [21, 22] in artificial saliva and NaCl 0.9%. The coated Ti50%Zr samples were thermally treated at $37^{O}C$ for 30 minutes in order to strengthen the apatite bonds.

2.2. Electrochemical Studies

Electrochemical behavior characterization was conducted with Voltalab (PGZ 301) with an assembly of three electrodes, using coated/uncoated samples as working electrode, Pt as counter electrode and Ag/AgCl as reference electrode. All experiments were done in SBF solution with a composition as it is presented in Table 1.

Table 1

Chemical composition of SBF solution

Compound	NaCl	$NaHCO_3$	KCl	$K_2PO_4 \cdot 3H_2O$	$MgCl_2 \cdot 6H_2O$	HCl 1M	$CaCl_2$	Na_2SO_4	$(CH_2OH)_3CNH_2$
Concentration (g/L)	7.996	0.350	0.224	0.228	0.305	40 mL	0.278	0.071	6.057

Polarization curves were registered between ± 200mV vs. free potential at a scan rate of 2mV/s. Various corrosion parameters were evaluated (i_{corr}- corrosion current, E_{corr}- corrosion potential, v_{corr}- corrosion rate).

Chronoamperometric measurements were performed in SBF solution at the potential 0.5 V vs. Ag/AgCl.

2.3. Surface Characterization- *SEM analysis*

Scaning electron microscopy (SEM Hitachi S-4160) was used to examine the chemical and surface morphology changes of coating that occurred after the immersion in simulated solutions.

2.4. Bioactivity test

To study the bioactivity, the coated samples were soaked in SBF which was proposed by Kokubo [18] at body temperature (37^{0} C) and pH: 7.4 for different periods up to 28 days. After the desired immersion time, the samples were taken out, washed with distilled water and dried at room temperature before SEM analyses.

3. Results and discussion

3.1. Initial tests

Tafel plots obtained in SBF solution for coated Ti50%Zr substrate (S0) sample and uncoated sample is presented in Fig.5. From the computed corrosion data (Table 2), it follows that in regard to current density and corrosion rate, the coated sample is stable.

Table 2

Corrosion parameters for coated and uncoatedTi50%Zr samples

Sample:	**i_{corr} (μA/cm^2)**	**E_{corr}(mV)**	**V_{corr}(μm/y)**	**Rp (Kohm·cm)**	**Ba (mV)**	**Bc(mV)**
Uncoated	0.6639	-718.8	28.840	51.61	136.0	-232.3
S0	0.1161	-552.7	5.045	252.45	230.2	-83.6

It was observed that the corrosion current density (i_{corr}) of the coated sample has a low value, proving the good protective properties of the electrodeposited coating. Moreover, the small value of the current density indicates that the film that was formed on the surface of the sample is stable and protective. On the other hand, the current density of the uncoated sample is higher indicating a decrease in protection abilities. Furthermore, the coated sample presents a Ba value higher than the absolute Bc value indicating that the sample has an inclination to passivity. In contrast to coated specimen, the uncoated one has an absolute Bc value higher than the Ba value meaning that the sample corrodes. Finally, Fig.5 shows the potentiodynamic curves for coated and uncoated samples representing an indication of the corrosion behavior of the samples.

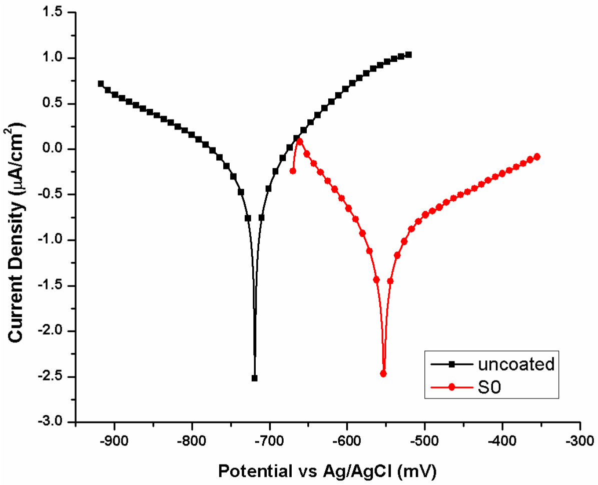

Fig. 5. Polarization curves for coated and uncoated TiZr samples

From the corrosion parameter presented at the Table 2 and the polarization curves at Fig. 5 can be noted that the coated sample is stable and offers a satisfactory protection.

3.2. Evolution of coatings

The essential requirement for an implant to bond to the living bone is the formation of bone-like apatite on its surface when implant is in the body. The evolution of S0 was investigated by immersing it in SBF for different periods of time (according to Kokubo tests) and the resulted samples are defined in Table 3.

Table 3

Immersion time of coated samples inSBF solution

Sample	S1	S2	S3	S4
Immersion Time (days)	3	7	14	28

The morphologies of samples S1-S4 are presented in Fig. 2:

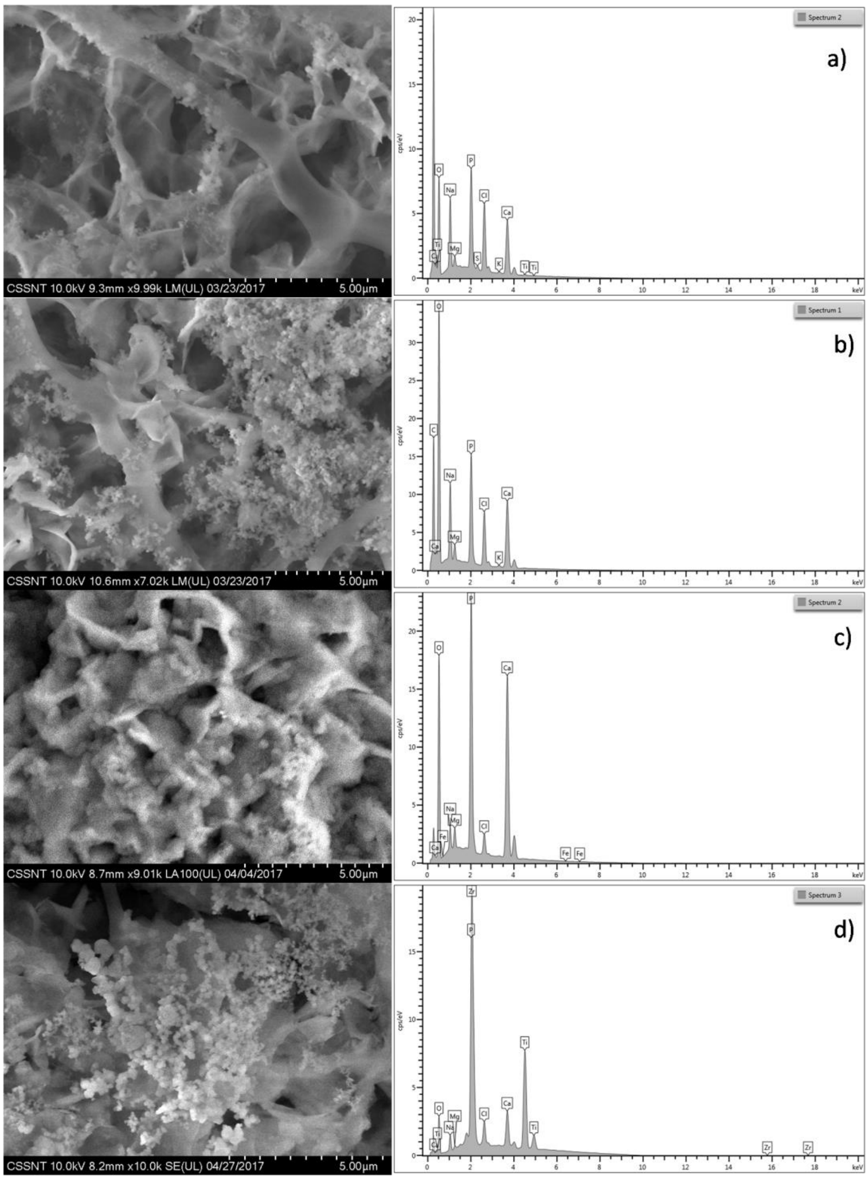

Fig. 2. SEM micrographies and EDX spectra for samples: a) S1; b) S2; c) S3; d) S4.

As is can be observed, structures similar to Ca-P are present on the surface coated with HAp-CS, but after 7 days of immersion the surface is not entirely covered (Fig. 2 a,b). As soaking time increased, many needle-like particles formed on the surface, and subsequently grew to micro-size crystals. Finally, layer clusters with petaloid shapes result after 28 days of immersion in SBF.

EDX analysis of the crystalline aggregate confirmed the presence of calcium and phosphorus in the layer deposition on TiZr/Hap:CS after different periods of soaking time in SBF. The examined Ca-P ratio of the aggregate range from 1.3 to 1.7. This means that in the beginning of the immersion period, the precursors of hydroxyapatite appear on the surface of the sample.

In order to investigate the compactness and stability of the Hap:CS films after the immersion time in SBF, chronoamperograms and Tafel plots were performed.

Fig. 3 shows the double logarithmic plots of chronoamperometric measurements performed in SBF solution at the potential 0.5V. The slopes of the lines correspond to k value in the following formula:

$$I = 10^{-(A + k \lg t)} \qquad (1)$$

where I is the current density, A is constant, t is time and k represents the slope of the double plot for potentiostatic polarization.

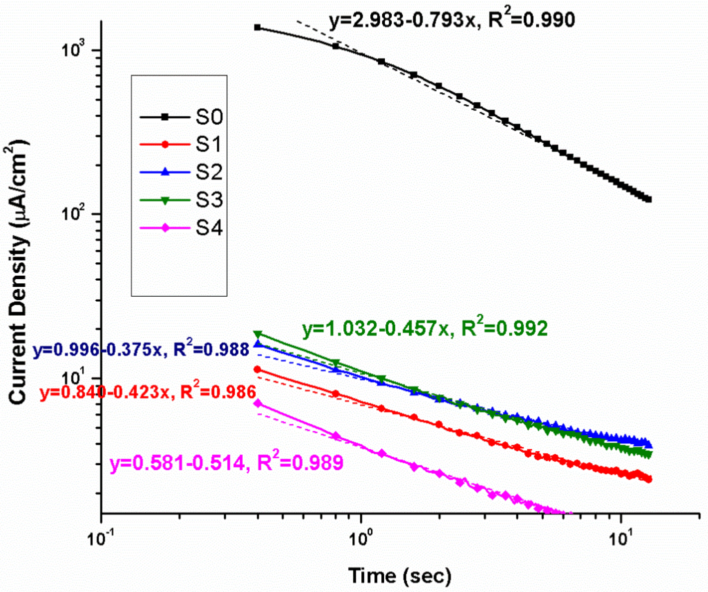

Fig. 3. Current vs polarization time recorded at 0.5V in SBF solution

According to the literature [23], when k = -1 indicates the presence of a compact protective passive film, while k = -0.5 is related to a porous film growing from a dissolution and precipitation process. Here, the k values were calculated and found as following: for S0 sample k = -0.793 ± 0.006, for S1 k = -0.423 ± 0.004, for S2 k = -0.375 ± 0.003, for S3 k = -0.457 ± 0.003 and for S4 k = -0.514 ± 0.004. Sample S2 shows the least compact Ca-P film on the surface evidenced also by the electrochemical parameters resulted from Tafel analyzes (Table 4). The experimentally determined k values suggest that after 28 days of immersion in SBF solution the samples have a porous surface film, whereas at 0 days of immersion the sample presents a more compact surface film.

The results are consistent with the SEM analysis showing that after 28 days of immersion the surface is covered with a porous hydroxyapatite film.

Tafel plots were also obtained for coated samples with different days of immersion in SBF solution. Fig. 4 shows the potentiodynamic curves for coated TiZr substrates immersed in SBF solution for a different periods of time.

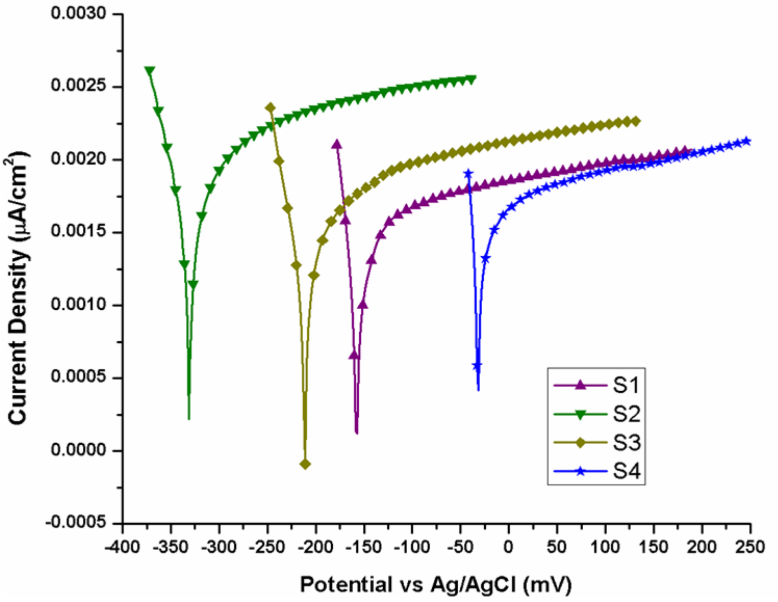

Fig.4. Polarization curves for coated TiZr samples immersed in SBF solution

These curves illustrate an indication of the corrosion behavior of the sample. In Table 4 are shown the results of the corrosion data, revealing that the fluctuation of corrosion current density (i_{corr}) is not correlated to the time interval of immersion in SBF solution, but is correlated with the compactness of the films. Furthermore, the current density of the immersed samples is lower than the uncoated one. The low values of the current density indicate that the formed film on the surfaces is stable and protective, especially for the samples S1 and S4 that were immersed for 3 and 28 days, respectively. Finally, from the following polarization curves it was found that the immersion time affects the corrosion resistance. For example, after 28 days of immersion in SBF (S4) the corrosion resistance was increased, whereas 7 days of immersion (S2) lowered the corrosion resistance.

Table 4

Corrosion parameters for coated Ti50%Zr samples with different days of immersion in SBF solution

Sample:	i_{corr} ($\mu A/cm^2$)	E_{corr}(mV)	V_{corr}($\mu m/y$)	Rp (Kohm·cm)	Ba (mV)	Bc(mV)
S1	0.0456	-156.3	1.979	621.72	798.3	-
S2	0.1427	-331.0	6.201	280.98	644.2	-
S3	0.0775	-211.4	3.365	540.03	874.7	-
S4	0.0457	-30.4	1.986	430.13	588.1	-

4. Conclusion

HAp/CS coatings with stable components ratio were successfully deposited on Ti50%Zr substrates by electrodeposition technique and the electrochemical stability and the bioactivity was evaluated. According to the corrosion rate (v_{corr}) obtained from the electrochemical characterization of the samples, sample S4 can be considered as the most stable one with a high resistance to corrosion and the lowest porosity level. Furhtermore, this specimen presents a less compact protective film. According to the bioactivity Kokubo test this coating is the most bioactive as well.

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