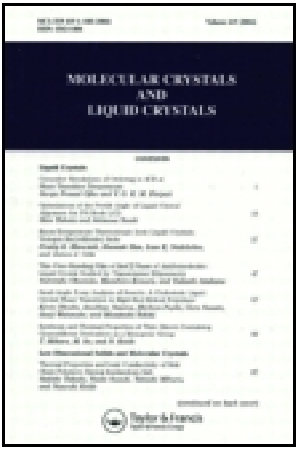

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# Biomimetic Hybrid Inorganic/Organic Coatings in the Increasing of the Integration Capacity of TiAlVZr Bioalloy

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# Biomimetic Hybrid Inorganic/Organic Coatings in the Increasing of the Integration Capacity of TiAlVZr Bioalloy

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*This paper will address key issues related to the synthesis, characterization and utilization of inorganic/organic hybrid coatings on TiAlVZr bioalloy to control adsorption at interface and the integration capacity of the implant. To enhance the integration capacity function of the biomaterial is necessary to control the composition and structure via the use of hybrid materials consisting of organic and inorganic biomimetic phases [1,2]. Such composite coatings mimic the structure of natural materials of tissues, in our case hydroxyapatite (HA) by association of bovine serum albumin (BSA) with calcium phosphates matrices. Calcium phosphate coating have been deposited on metal substrates by electrochemical method.*

**Keywords:** albumin; bioalloy; hybrid materials; hydroxyapatite (HA)

## INTRODUCTION

This paper will address key issues related to the synthesis, characterization and use of inorganic/organic hybrid coatings on TiAlVZr bioalloy to control the adsorption at interface and integration capacity of the implant. One approach to enhance the integration capacity function of the biomaterial is to control the composition and structure via the use of hybrid materials consisting of organic and inorganic biomimetic phases [1,2]. Such composite coatings mimic the structure of natural materials of tissues, in our case hydroxyapatite by association of bovine serum albumin (BSA) with calcium phosphates matrices.

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## EXPERIMENTAL PARTS

Calcium phosphate coating have been deposited on metal substrates by electrochemical method [3]. The electrolyte solution consisted of 0.042 mol/L $Ca(NO_3)_2$ and 0.025 mol/L $NH_4H_2PO_4$. This solution has a molar ratio of Ca to P as 1.67. The cathodic polarization and deposition were carried out with a Voltalab 40 potentiostat/galvanostat. TiAlVZr disks were used as cathode, a Pt plate as counter-electrode, and a saturated calomel electrode as reference electrode. Cathodic polarization was conducted from open circuit potential to $-3$V (vs. SCE) with a rate of 0.6 V/h. Coating were deposited at current densities of 1–20 mA/cm$^2$ for 50 min at room temperature and pH = 4. After deposition, the electrode was placed one by one in various concentration of BSA (100, 1000, 10000, 100000 ng/mL) at 37°C for 12 h. Coated plates were then rinsed with demineralized water and dried at 220°C.

Fourier transformed infrared spectroscopy (FTIR) using a FTIR Jasco 620 was used to determine the structure of the coating by scratching then KBr pellet. Topography studies were accomplished by the using scanning electronic microscopy with an Environmental Scanning Electron Microscope FEI/Phillips XL30 ESEM with an energy dispersive X-ray analysis module (EDAX) [4].

After the surface preparation, each specimen was cleaned in deionized water for 5 min and dried in air. Modified Tani-Zucchi synthetic saliva containing 1.5 g/L KCl, 1.5 g/L $NaHCO_3$, 0.5 g/L $NaH_2PO_4$, 0.5 g/L KSCN, 0.9 g/L lactic acid, was used as the test environment [5].

The corrosion measurements were conducted in the following sequence:

(a) Linear polarization was conducted from $-10$ to $+10$ mV around the open circuit potential at a rate of 0.1 mV/s in the aerated medium; the corrosion rate ($i_{corr}$) of the samples was determined according to the Stern-Geary equation [6].

$$i_{\mathrm{corr}} = \frac{\beta_a \beta_c}{2.3 R_p(\beta_a + \beta_c)}$$

where $R_p$ is the polarization resistance, $\beta_a$ and $\beta_c$ are the anodic and cathodic Tafel slopes;

(b) Cyclic polarization were performed using Voltalab 40 equipment with Voltamaster program; the samples were immersed for 15 min in electrolyte prior to start the polarization scan at $-800$ mV; The scan was initiated in the nobler direction at a scan rate of 2 mV/s.

# RESULTS AND DISCUSSION

## Coating Deposition, Structure and Morphology

The cathodic polarization curve of TiAlVZr substrate in Tani-Zucchi saliva is showed in Figure 1. The cathodic curve presents 3 domains with the corresponding reactions.

Domain I (−0.4 V): reduction of oxygen:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

Domain II (from −0.4 V to −1.6 V): reduction of $H_2PO_4^-$ and $HPO_4^{2-}$

$$2H_2PO_4^- + 2e \rightarrow 2HPO_4^{2-} + H_2$$

$$HPO_4^{2-} + 2e \rightarrow 2PO_4^{3-} + H_2$$

Domain III (from −1.6 to −3.0 V): reduction of water

$$2H_2O + 2e \rightarrow H_2 + 2OH^-$$

Positive $Ca^{2+}$ ions migrate to cathodic TiAlVZr substrate and could react with $PO_4^{3-}$ and $OH^-$ ions formed on surface to synthesize the hydroxyapatite coating.

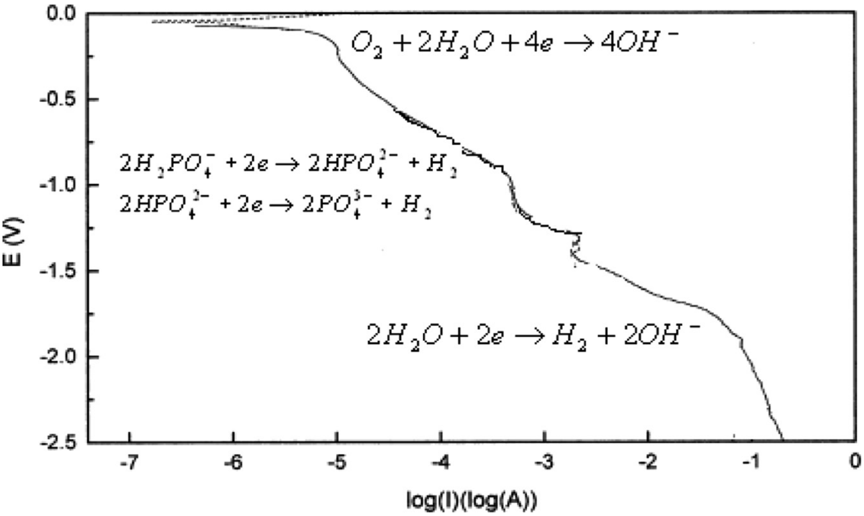

**FIGURE 1** Cathodic polarization curve for TiAlVZr substrate in Tani-Zucchi saliva.

According with literature data [7] the following precipitation reaction equilibrium has to be taken into consideration:

$$10Ca^{2+} + 6PO_4^{3-} + 2OH^- \leftrightarrow Ca_{10}(PO_4)_6(OH)_2$$

$$3Ca^{2+} + 2PO_4^{3-} + nH_2O \leftrightarrow Ca_3(PO_4)_2 \cdot nH_2O$$

$$8Ca^{2+} + 6HPO_4^{2-} + 5H_2O \leftrightarrow Ca_8H_2(PO_4)_6 \cdot 5H_2O + 4H^+$$

$$Ca^{2+} + HPO_4^{2-} + 2H_2O \leftrightarrow CaHPO_4 + 2H_2O$$

The HA coated electrode was first immersed in a solution containing 100 ng/mL BSA solution at 37°C for 12 h to enhance protein adsorption, and then rinsed and dried. This sequence was repeated for 1000, 10000, 100000 ng/mL BSA solution. At the end, the coated samples were rinsed with demineralized water and dried at 220°C.

FTIR analysis (Fig. 2) of the inorganic coating (HA) shows the presence of the carbonate group at around 1430 $cm^{-1}$, hydroxyl group at around 3410 and 1640 $cm^{-1}$ and phosphate group at 600 or 565 $cm^{-1}$ representing $\nu_4$ O–P–O binding vibration [8]. For TiAlVZr coated with albumin, apatite composite, specific bands at 1028 and 1098 $cm^{-1}$, seem to agree with the formation of a well-crystallized apatite. A more detailed analysis permits to conjecture the presence of amide I (1654 $cm^{-1}$) and amide II (1542 $cm^{-1}$) component. Carbonated bands

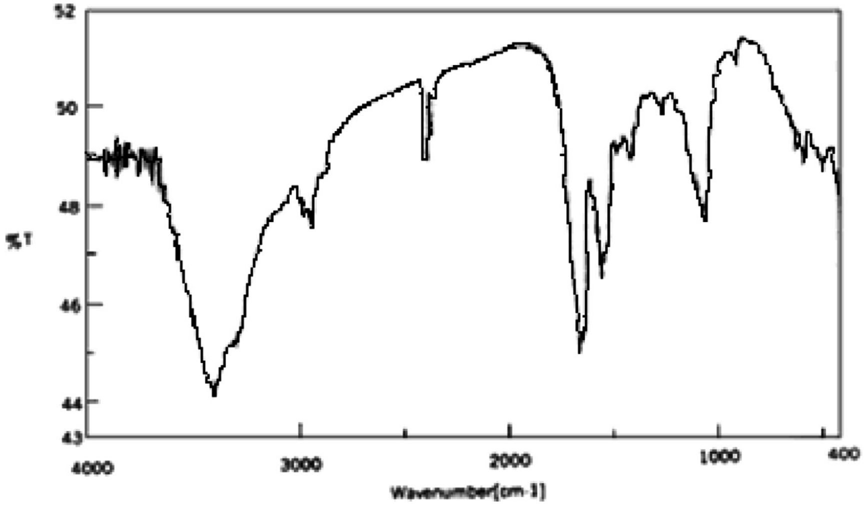

**FIGURE 2** FTIR analysis of hybrid inorganic/organic coating.

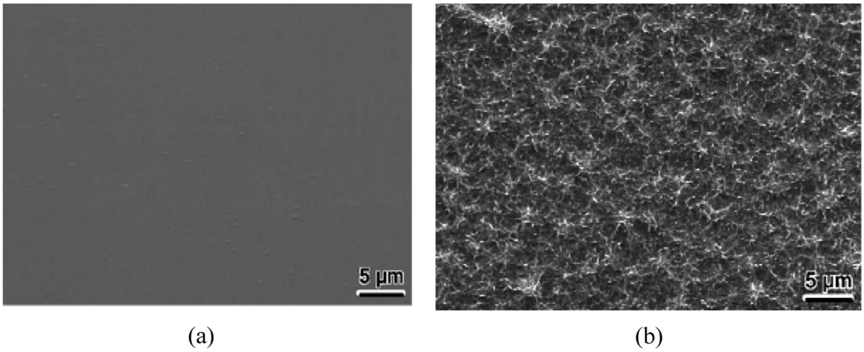

**FIGURE 3** SEM imagine of: a) untreated TiAlVZr; b) TiAlVZr coated with hybrid coating.

have been detected at 875, 1420 and 1453 cm$^{-1}$. Molecular and adsorbed water bands are also discerned at 1583 and 3400 cm$^{-1}$.

SEM image (Fig. 3) for uncovered TiAlVZr alloy (a) and TiAlVZr coated with hybrid inorganic/organic coating (b) revealed that a uniform layer of Ca–P had been deposited all over surface.

The composition of thin hybrid layer was obtained from the EDAX spectrum (Fig. 4); this spectrum confirms that the depositions on TiAlVZr surface were composed of calcium and phosphorous elements and give evidence of C and N in the structure of thin layer. The source

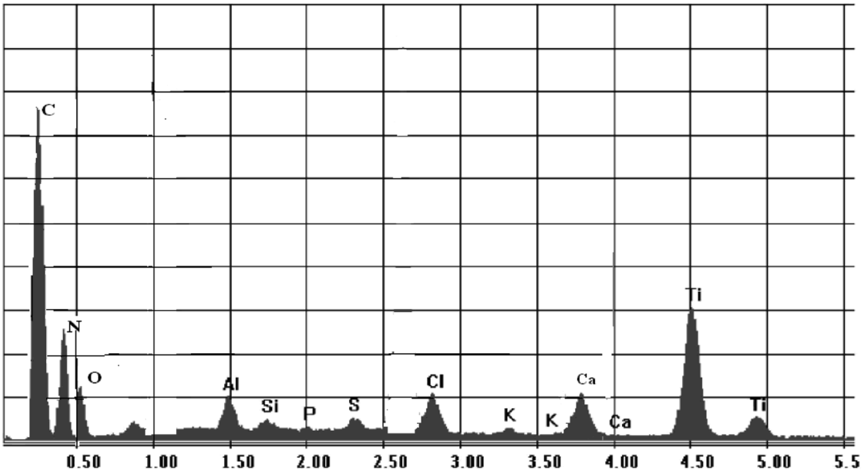

**FIGURE 4** EDAX spectrum for hybrid coating.

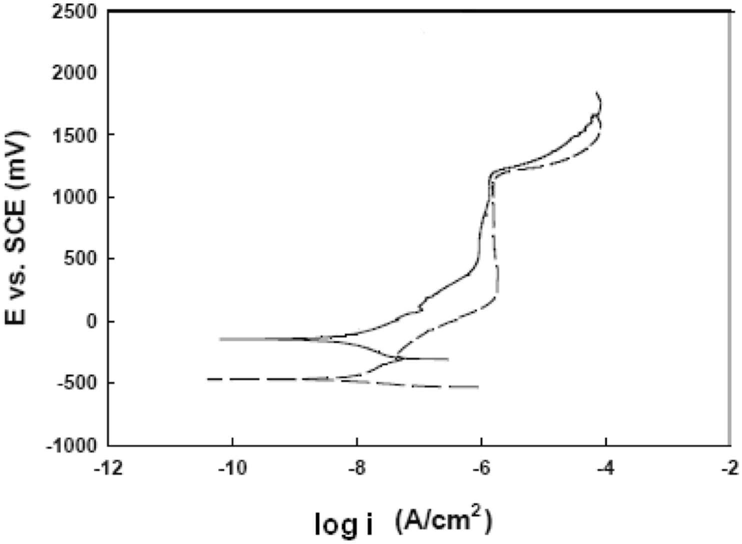

**FIGURE 5** Potentiodynamic anodic polarization curves for uncoated (–) and coated (–) TiAlVZr alloy.

of C and N elements is the interaction between the inorganic and organic component during the precipitation process [9].

## Corrosion Behavior of TiAlVZr Bioalloy

Figure 5 shows the behavior of the bare and coated TiAlVZr bioalloy in artificial saliva. A distinctly larger passive region with lower passive current density can be observed for the coated surface, confirming the beneficial effect of the biomimetic hybrid inorganic/organic coating.

The electrochemical parameters for uncoated and coated TiAlVZr alloy are listed in Table 1. Lower $R_P$and higher $i_{corr}$ values for uncoated alloy suggest that its surface is less corrosion resistant than coated surface.

**TABLE 1** Electrochemical Parameters for Uncoated and Coated TiAlVZr Alloy in Tani-Zucchi Synthetic Saliva

| Samples | $E_{corr}$ (mV) | $i_{corr}$ (nA/cm$^2$) | $R_p$ (M$\Omega$ cm$^2$) | $V_{corr}$ (mm/year) |
|---|---|---|---|---|
| TiAlVZr coated | $-110$ | 68 | 4.5 | $0.78 \times 10^{-3}$ |
| TiAlVZr uncoated | $-135$ | 185 | 1.25 | $2.14 \times 10^{-3}$ |

## CONCLUSIONS

The results suggest that the method used in this work can be successfully applied to obtain fast deposition of uniform, hybrid inorganic/organic coating on TiAlVZr alloy surface. The hybrid coating has a benefic effect on electrochemical stability of studied bioalloy.

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