

Infrared and ESEM technique in supporting Ti and Ti-Al-V alloy behaviour in Afnor and Tani-Zucchi solutions

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The aim of the paper is the study of adsorption process in simulated artificial saliva after 5 months immersion of implant dental biomaterial. The simulated artificial saliva are Afnor and Tani-Zucchi solutions and implant materials are Ti and Ti-Al-V. Infrared (IR) and Environmental Scanning Electron Microscopy (ESEM) methods were performed in order to identify the structure and composition of the film reformed after immersion in saliva and corrosion process. Despite of good corrosion resistance of Ti and Ti-Al-V alloy which was put in evidence using electrochemical methods [1-3], Ti and Ti-Al-V immersed in simulated medium of Afnor and Tani-Zucchi for longer time noticed small effects of a local corrosion as an intercrystalline type. The IR and ESEM methods confirm the presence of phosphate anion in the solutions as a result of an absorption process and topological changes on the samples surface after immersion in Afnor and Tani-Zucchi media, indicating the presence of Na and Cl elements existing in composition of both artificial saliva.

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Keywords: Titanium; Ti-Al-V alloy, Artificial saliva

1. Introduction

Taking into account that dental implants are substitutes tooth roots that provide essentially the same function as natural tooth roots, stimulating bone growth, an important research is devoted to understanding the behaviour of various implant in simulated saliva in order to prevent their deterioration [4, 5]. This deterioration of dental implant integrity can be produced when the degradation process is sufficient severe, frequently in the presence in the oral cavity of the organic or inorganic ions resulted after the mastication process, when the first stage of the digestion of the food is taken place. However, to avoid the presence of toxic products of corrosion are very important in knowing the corrosion resistance of the metallic biomaterials before their use as implant in dentistry [6-9]. Titanium and its alloys have an important resistance to corrosion process, induced by surface titanium oxide as a passive film, in all biological environments, including saliva. Among most important properties of titanium and the Ti-Al-V alloy are: the chemical stability and the integrity of the oxide film; the passivity of the surface material and the property of the inert material in biological fluid; the good integration in the smooth and strong tissues, without a major non positive answer from the human body [10-14]. Characterization of electrochemical biointerface is first of all based on adsorption of protein and various ions as most important phenomenon [15-16] and the present paper is an argument for such processes.

2. Experimental

Materials used are Romanian Ti and Ti-Al-V alloy from Bucharest IMNR Institute with composition presented in a previous paper [20, 21]. The surface preparation involves followings operations: abrasion,

chemically polished in 20 % HNO₃ + 3 % HF from 10 minutes, degreased in boiling benzene from 5 minutes and thoroughly rinsed with tap and distilled water. The biological tested environments were two kind of artificial saliva Afnor and Tani-Zucchi [22].

Compositions of the respectively simulated artificial saliva are as following:

Composition of artificial Afnor saliva (Af): NaCl 0.7 g/L; KCl 1.2 g/L; Na₂HPO₄ 0.26 g/L; NaHCO₃ 1.5 g/L; KSCN 0.33 g/L; urea 1.3 g/L.

Composition of artificial Tani-Zucchi saliva (TZ): KCl 1.5 g/L; NaHCO₃ 1.5 g/L; NaH₂PO₄ 0.5 g/L; KSCN 0.5 g/L; lactic acid 0.9 g/L.

The experiments were performed using the following techniques: Infrared Spectroscopy method (IR) - FT-IR JASCO Model 620 system with a computer interface [23] and Scanning Electron Microscopy (SEM) - FEI / Phillips XL30 ESEM Model scanning microscopy method (ESEM) [24].

3. Results and discussion

The electrochemical behaviour of Ti and Ti-Al-V biomaterials in simulated artificial saliva Afnor and Tani-Zucchi was discussed in a previous paper [1-3] and a good stability was established for both of them. After open circuit potential determinations a change in the composition and structure of the film was observed due to the adsorption phenomenon at the interface. The infrared spectra presented in Figs. 1 ÷ 4 are arguments for the new composition of the films (on Ti and titanium alloy) reformed after immersion in saliva and corrosion process. The infrared analysis was performed using samples introduced in KBr pellet.

The important anions from simulated artificial saliva existing on titanium samples after immersion are presented in the Table 1 and Fig. 1 and 2:

Table 1. The bonded appears in the IR spectrum.

Physiologic medium	ν [cm^{-1}]	Type of bonds
Afnor	1084	PO_4^{3-}
	400 -650	P-O-
	3427	vOH associated
Tani-Zucchi	1087	PO_4^{3-}
	420-500	P-O-
	3433	vOH associated

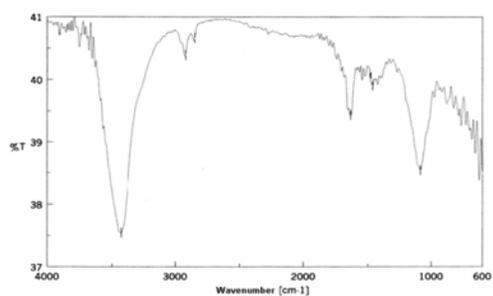


Fig. 1. Infrared spectra of film formed on Ti in Afnor solution.

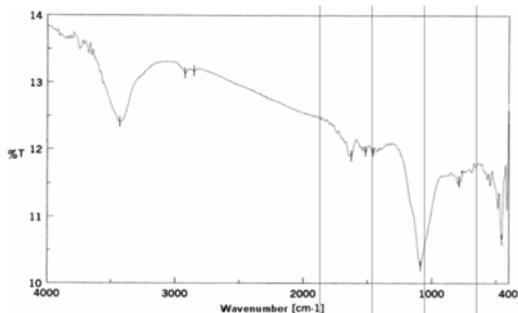


Fig. 2. Infrared spectra of film formed on Ti in Tani-Zucchi solution.

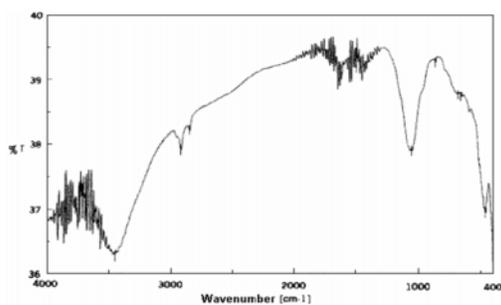


Fig. 3. Infrared spectra of film formed on Ti-Al-V alloy in Afnor solution.

After immersion of titanium alloy in simulated medium, bonded phosphate appears in the IR spectrum (Figs. 3, 4) at 467 cm^{-1} and 1057 cm^{-1} and adsorption band

related to the OH of hydrogen bonding is observed at 3449 cm^{-1} . The presence both of $(\text{H}_2\text{PO}_4)^-$ and $(\text{HPO}_4)^{2-}$ groups in artificial saliva composition probably determinate the phosphate adsorption [25].

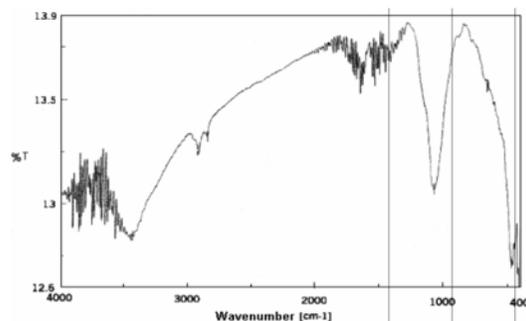


Fig. 4. Infrared spectra of film formed on Ti-Al-V alloy in Tani-Zucchi solution.

The phosphate anions absorption existing in samples collected from films surfaces was put in evidence also using surface analysis. ESEM determinations are arguments for the modification of surfaces with the help of spectrum for emission in X-ray. Ti and Ti-Al-V immersed in simulated medium of Afnor and Tani-Zucchi noticed small effects of a local corrosion as an intercrystalline type.

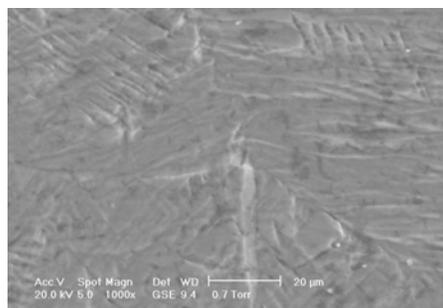


Fig. 5. ESEM image of surface titanium sample after immersion for 5 month in Afnor solution.

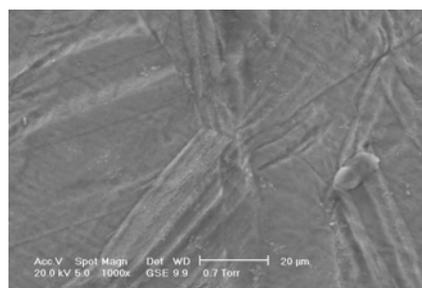


Fig. 6. ESEM image of surface titanium sample after immersion for 5 month in Tani-Zucchi solution.

Ti presented effects of corrosion at the limit of the bands of skid (inside of grain) and the attack to limit of grain, more visible after immersion in artificial saliva Tani-Zucchi solution (Fig. 5 and 6).

The Figure 7 and Figure 8 represent the variation of chemical elements from the samples of Ti after 5 months immersion in solution and the presence of Na and Cl elements who exist in composition of artificial saliva can be seen.

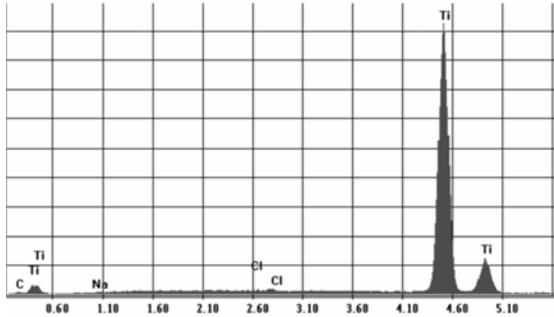


Fig. 7. Spectrum for emission in X-ray from Ti before and after immersed 5 months in Afnor solution.

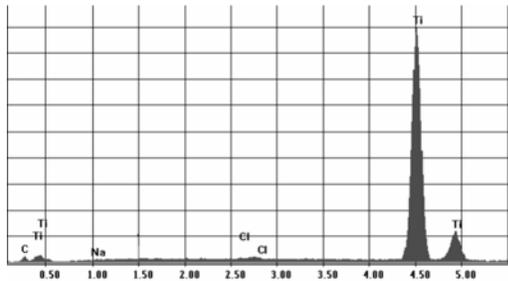


Fig. 8. Spectrum for emission in X-ray from Ti before and after immersed 5 months in Tani-Zucchi solution.

The compositions of passive layers of the surface of titanium samples immersed in simulated oral cavity solution are presented in Table 2. According to Table 2 the amount of titanium released in environment is more important in the case of Tani-Zucchi saliva.

Table 2. The result of chemical analyse of metallic biomaterials surface with the equipment of microscopy ESEM.

Titanium	wt [%]	At [%]
Ti immersed 5 month in Afnor	96.86	89.87
Ti immersed 5 month in Tani-Zucchi	88.16	70.29

Titanium alloy (Ti-Al-V) is subject of the same effect of corrosion at the limit of the bands of skid (inside of grain) and the attack to limit of grain, more visible after immersion in artificial saliva Tani-Zucchi solution (Fig. 9 and 10).

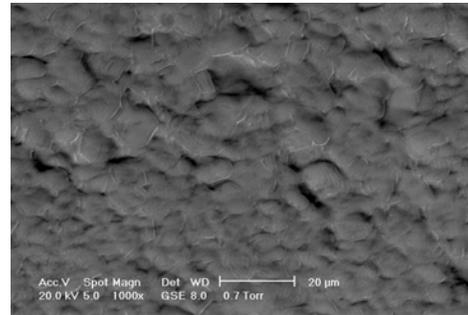


Fig. 9. ESEM image of surface titanium alloy sample after immersion for 5 month in Afnor solution.

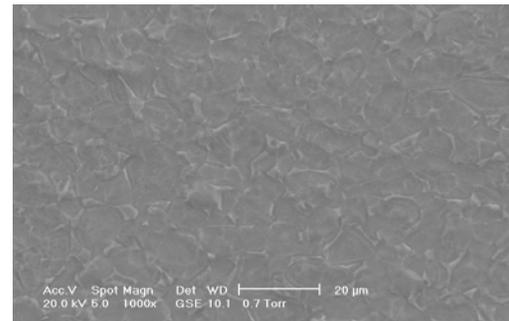


Fig. 10. ESEM image of surface titanium alloy sample after immersion for 5 month in Tani-Zucchi solution.

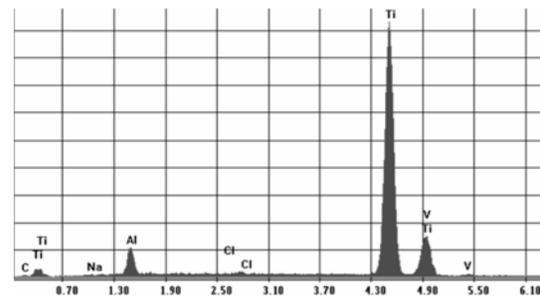


Fig. 11. Spectrum for emission in X-ray from Ti-Al-V before and after immersed 5 months in Afnor solution.

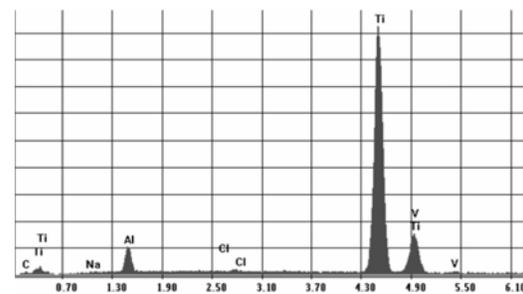


Fig. 12. Spectrum for emission in X-ray from Ti-Al-V before and after immersed 5 months in Tani-Zucchi solution.

The Figs. 11 ÷ 12 and Table 3 are expressions of the variation of chemical elements from the samples of Ti-Al-V after 5 months immersion in simulated oral cavity

solutions. As in titanium case, the presence of initial elements and also Na and Cl elements existing in composition of artificial saliva are put in evidence.

The elements compositions of the passive layers at the surface of Ti-Al-V samples immersed in artificial saliva are presented in Table 3:

Table 3. The result of chemical analyse of metallic biomaterials surface with the equipment of microscopy ESEM.

Elements	wt [%]			At [%]		
	Ti	Al	V	Ti	Al	V
Ti-Al-V immersed 5 month in Afnor	88.52	6.18	2.12	78.49	9.73	1.77
Ti-Al-V immersed 5 month in TZ	88.41	5.74	2.08	77.72	8.96	1.72

The chemical analysis after immersion for Ti-Al-V in both studied saliva is almost similar, and this is an argument for the same amount of ions release in the environment.

4. Conclusions

1. The infrared spectroscopy method (IR) confirms the presence of phosphate anion in the solutions as a result of an absorption process.

2. Topological changes on the samples surface after immersion in Afnor and Tani-Zucchi media indicate the presence of Na and Cl elements existing in composition of both types of artificial saliva.

3. The chemical analysis after immersion for Ti indicate an amount of titanium released in environment more important in the case of Tani-Zucchi saliva, but for Ti-Al-V in both studied saliva behaviour is almost similar.

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