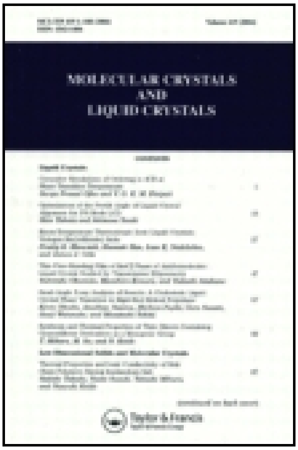

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The Methionine Influence on Artificial Saliva Oxidant Character

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The Methionine Influence on Artificial Saliva Oxidant Character

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The goal of this article is to establish the influence of methionine – an important amino acid from human body which exists in different aliments – on the oxidant character of artificial saliva in the presence of a titanium alloy implant. As titanium alloy was proposed Ti6Al4 V with a surface passivated using anodization or treated in acids. As simulated artificial saliva were used well known composition Afnor and Carter-Brugirard solutions.

Keywords: acid treatment; anodization; methionine; titanium alloy

INTRODUCTION

In dental domain an important research is devoted to understanding the behaviour of various bioimplant in simulated saliva in order to prevent their deterioration [1–4], and this deterioration of dental implant integrity can be produced after the mastication process. However, to avoid the presence of toxic products of corrosion are very important to know the corrosion resistance of the metallic biomaterials before their use as implant in dentistry [5,6] and the treatment method for this biomaterial before the applications. It is know that 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 [7,8]. The influence of the aliments components on the film stability became recently [9–11] a subject of interest.

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EXPERIMENTAL PART

Materials and Methods

The TiAlV samples elaborated in IMNR Bucharest (Ti-6Al-4 V alloy: max 0.08% C, 5.5–6.5% Al, max 0.25% Fe, max 0.0125% H_2, max 0.05% Mn, 0.13% O_2, 3.5–4.5% V, 86–88% Ti) were provided in cyclic forms after infusion. First, the TiAlV with a mirror surface were washed with distilled water and treated in two different ways as following:

1. chemically polished in HNO_3 (20%) + HF (3%) for 10 minutes, degreased in boiling benzene from 5 minutes and thoroughly rinsed with tap and distilled water (I);
2. passivated using anodization (II).

The biological tested environments were two kind of artificial saliva Afnor and Carter-Brugirard with known composition from literature [12,13]:

- Afnor (Af): 0.70 g/L NaCl, 1.20 g/L KCl, 0.26 g/L Na_2HPO_4, 1.50 g/L $NaHCO_3$, 0.33 g/L KSCN, 1.30 g/L urea;
- Carter-Brugirard (CB): 0.70 g/L NaCl, 1.20 g/L KCl, 0.26 g/L Na_2HPO_4, 1.50 g/L $NaHCO_3$, 0.33 g/L KSCN, 0.20 g/L K_2HPO_4, 0.13 g/L urea.

For the simulation presence of an aliment in the oral cavity, in biological tested environmental was added the methionine (Met) which exists in different aliments.

The experiments were performed using the following techniques:

- open circuit potential measurements using METRIX 20 system;
- cyclic polarisation experiments using Voltalab 40 PGZ 301 system with a computer interface – soft VoltaMaster 4, from −0.8 V to +4 V for anodic polarisation;
- variation of pH solutions in time using inoLab pH/Cond 720, WTW 82362 Weilhein;
- chemiluminescence's determinations using Turner Designes TD 20/20 chemiluminometer with computer interface as a complementary method in evaluation redox properties of the system.

The temperature of determination was 37°C, and the exposure surface biomaterial used in experiments and immersed into artificial medium was to 1 cm^2.

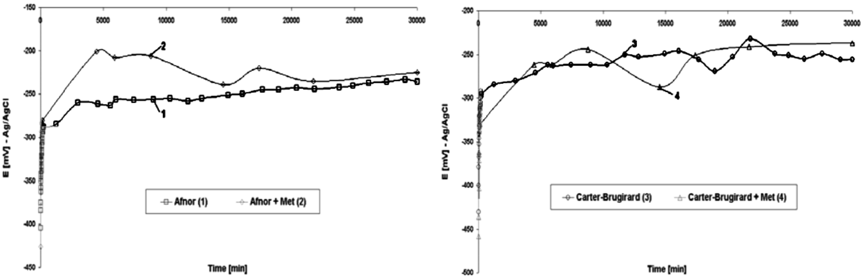


FIGURE 1 The variation in open circuit potential of TiAlV alloys (I) immersion in artificial saliva: Af (1); Af + Met (2); CB (3); CB + Met (4). Time of immersion 21 days, $c_{Met} = 10^{-5}$ M.

RESULT AND DISCUSSIONS

The variation of open circuit potential of TiAlV in time in artificial solutions (Figs. 1 and 2) shows that the oxide passive films which exist on the surface of titanium suffers a partial dissolution and repassivation phenomenon, and after a period of time a trend to steady-state in all studied cases, was observed.

Titanium alloy provides excellent corrosion resistance due to the TiO_2 protective oxide film. The representations of cyclic voltametry curves for TiAlV in different types of simulated artificial saliva are presented in Figures 3 and 4.

In the case of the treatment with a mixture of acids (I), the presence of methionine induces a larger passive domain (more than 1000 mV)

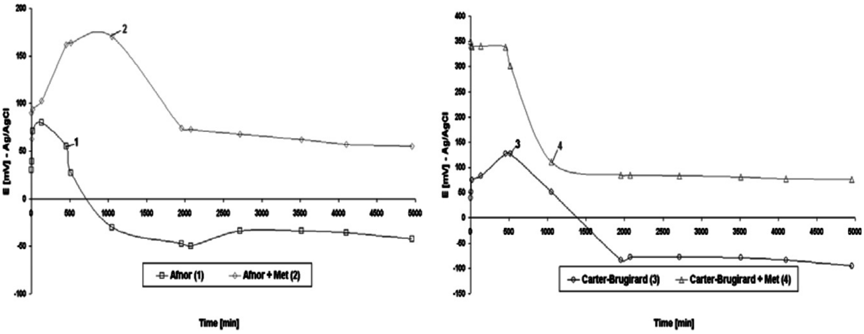


FIGURE 2 The variation in open circuit potential of TiAlV alloys (II) immersion in artificial saliva: Af (1); Af + Met (2); CB (3); CB + Met (4). Time of immersion 4 days, $c_{Met} = 10^{-5}$ M.

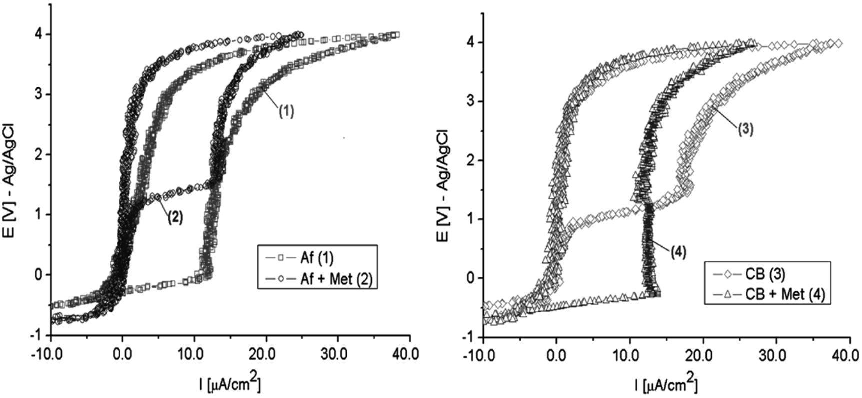


FIGURE 3 Cyclic polarization curves for the TiAlV electrodes (I) immersed in artificial saliva: Af (1); Af + Met (2); CB (3); CB + Met (4). The rate of scan was 2 mV/s, $c_{Met} = 10^{-5}$ M.

comparing to the value of the passive domain in artificial saliva without methionine. Also, the corrosion density and corrosion rate are smaller in the methionine presence than in the initial environment of oral cavity, the values being as followings: $0.49\,\mu A/cm^2 \rightarrow 0.06\,\mu A/cm^2$ for Af/Af + Met ($c_{Met} = 10^{-5}$ M); $0.44\,\mu A/cm^2 \rightarrow 0.13\,\mu A/cm^2$ for CB/CB + Met ($c_{Met} = 10^{-5}$ M), respectively $8.15 * 10^{3}$ mm/year $\rightarrow 1.01 * 10^{-3}$ mm/year for Af/Af + Met ($c_{Met} = 10^{-5}$ M);

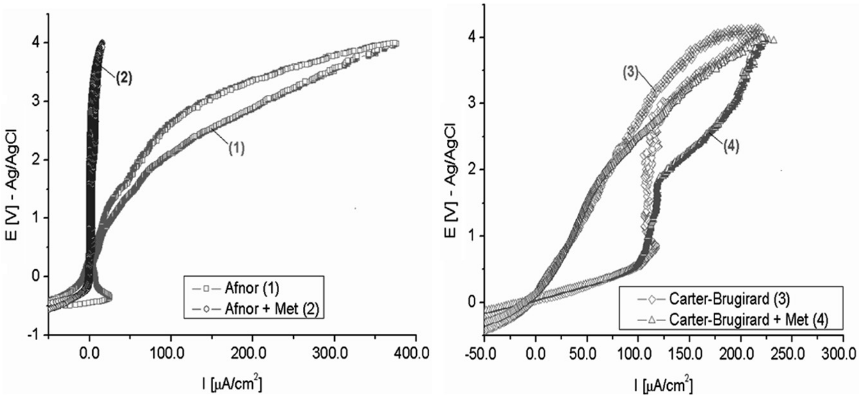


FIGURE 4 Cyclic polarization curves for the TiAlV electrodes (II) immersed in artificial saliva: Af (1); Af + Met (2); CB (3); CB + Met (4). The rate of scan was 2 mV/s, $c_{Met} = 10^{-5}$ M.

$7.32 * 10^{-3}$ mm/year → $2.15 * 10^{-3}$ mm/year for CB/CB + Met ($c_{Met} = 10^{-5}$ M) (Fig. 3).

After the anodized treatment of alloy surface (II), the passive current and the corrosion density current present smaller values than in the case of the treatment with acids and this is an argument for a better corrosion resistance (Fig. 4).

Using different concentration of methionine (10^{-3} M, 10^{-5} M, 10^{-7} M) in the artificial saliva it was found that the increase of the concentration of the methionine increase the speed of corrosion of Ti-Al-V biomaterial treated (I) and (II) (for treatment (I): $3.82 * 10^{-3}$ mm/year → $0.94 * 10^{-3}$ mm/year for Af + Met ($c_{Met} = 10^{-3}$ M)/Af + Met ($c_{Met} = 10^{-7}$ M); $4.83 * 10^{-3}$ mm/year → $2.03 * 10^{-3}$ mm/year for CB + Met ($c_{Met} = 10^{-3}$ M)/CB + Met ($c_{Met} = 10^{-7}$ M)).

The electrochemical parameters values (Table 1) of TiAlV alloys chemically polished in HNO_3 (20%) + HF (3%) (I) or passivated using anodization (II) indicate a better evolution in all cases. It is very important to point out that in both situations for this study, the titanium alloys do not present the local corrosion phenomenon associated with breakdown of the passive film.

The variation of pH solution versus time in the same conditions is presented in Figure 5.

The acidifying effect of methionine introduces in the simulated oral bioliquid cavity used in these experiments for analyzed the titanium alloy used as implant, determinates a decrease of basic pH of solutions. In this case the pH value domain is > 7.2, comparative with the pH of the solution without methionine (pH > 8.2).

The chemiluminescence method sustains electrochemical data regarding the influence of the methionine as an antioxidant (Fig. 6).

TABLE 1 The TiAlV Electrochemical Parameters in Artificial Saliva Solutions, from the Cyclic Polarization Curves

Electrode	Solutions	Passive domain [mV]	I_{corr} [μA/cm^2]	E_{corr} [mV]	$V_{corr} * 10^3$ [mm/year]
TiAlV treated in HNO_3 (20%) + HF (3%) (I)	Afnor	> 2000	0.49	−285.2	8.15
	Afnor + Met	> 1000	0.06	−129.3	1.01
	Carter-Brugirard	> 1000	0.44	−211.5	7.32
	Carter-Brugirard + Met	> 3000	0.13	−494.8	2.15
TiAlV anodized (II)	Afnor	> 2000	0.25	−448.7	4.14
	Afnor + Met	> 3000	0.16	−131.3	2.65
	Carter-Brugirard	> 2000	0.09	28.5	1.49
	Carter-Brugirard + Met	> 1000	0.03	58.5	0.50

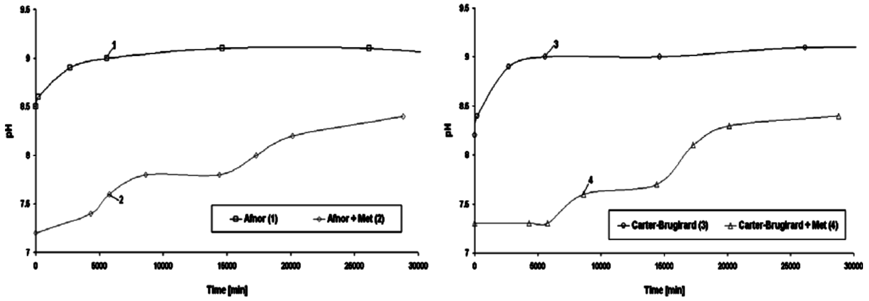
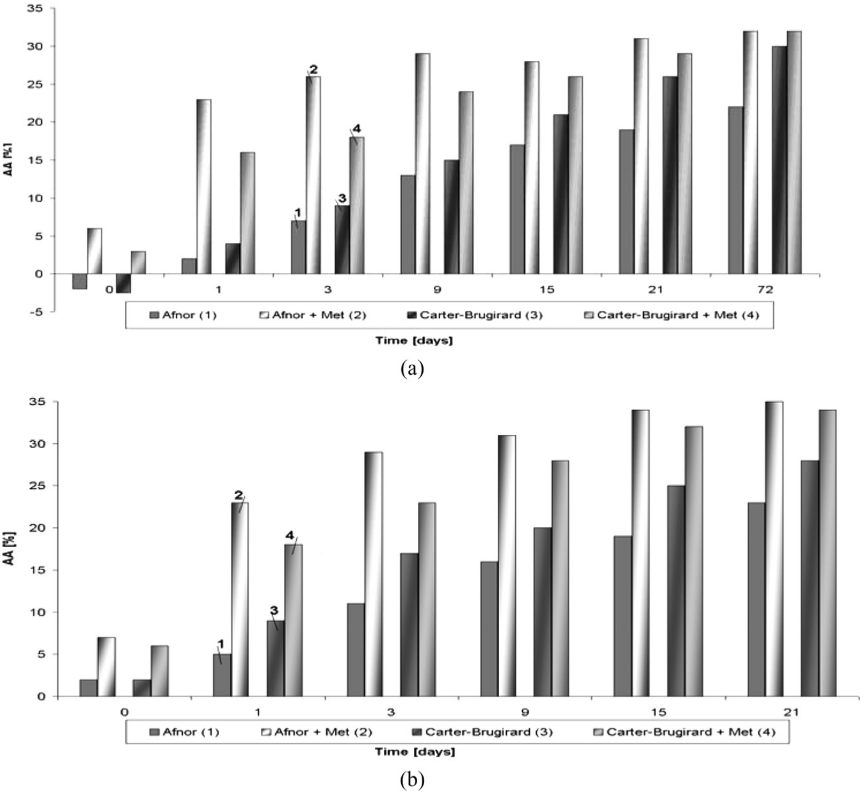


FIGURE 5 The variation of pH solution in time where TiAlV alloys (I) was immersion: Af (1); Af + Met (2); CB (3); CB + Methionine (4).



(a)

(b)

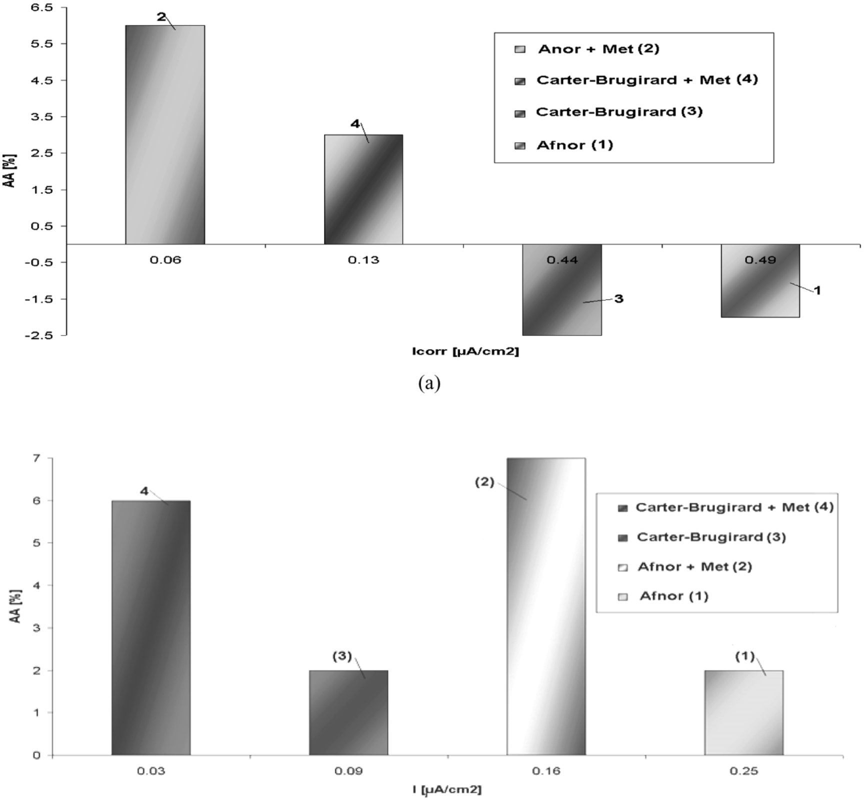
FIGURE 6 The variation in time of antioxidant activity of the artificial saliva with immersed TiAlV samples: (a) acids treatment samples (I); (b) anodized samples (II).

The antioxidant characters present the antioxidant activity efficiency of solutions in all cases according to following range:

$$AA_{Af+Met} > AA_{CB+Met} > AA_{CB} > AA_{Af}$$

The methionine presence induces an increase of the antioxidant character.

The electrochemical method presented the important parameters as corrosion density and corrosion rate which characterized the biomaterial implant stability and this data were correlated with the antioxidant activity as the important parameter which characterized the biological simulated environmental. This correlation between the electrochemical/nonelectrochemical data is presented in Figures 7a and 7b.



(a)

(b)

FIGURE 7 The correlation AA = f (I_{corr}) in artificial saliva solution with immersed TiAlV electrodes: (a) acids treatment samples (I); (b) anodized samples (II).

According to Figure 7, the presence of methionine in simulated oral cavity for short time, induces a better stability of immersed biomaterial in both cases of treated surface.

It is well known that the most important event at the interface implant/bioloquids is adsorption, [14] but diffusion is also taken place. Taking into account that the kinetic constants computed from chemiluminescent signal are not very small ($6.2 * 10^{-2}\,\mathrm{sec}^{-1}$ in Afnor, $7.3 * 10^{-2}\,\mathrm{sec}^{-1}$ in Afnor + Met, $7 * 10^{-2}\,\mathrm{sec}^{-1}$ in Carter-Brugirard, $7.4 * 10^{-2}\,\mathrm{sec}^{-1}$ in Carter-Brugirard + Met), probably the diffusion is less important than adsorption.

CONCLUSIONS

1. In the case of the treatment with a mixture of acids, the presence of methionine induces a larger passive domain (more then 1000 mV) comparing to the value of the domain in artificial saliva without methionine. Also, the corrosion density and corrosion rate are smaller in the methionine presence than in the initial environment of oral cavity.
2. After the anodized treatment of alloy surface, the passive current and the corrosion density current present smaller values comparing to the case of acids treatment.
3. Chemiluminescence method sustains electrochemical data regarding the influence of the methionine as an antioxidant. The correlation between the electrochemical results (I_{corr}) and chemiluminescence results (AA) indicated the evolution of the antioxidant character in the initial moment better for Carter-Brugirard solution.

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