

# Electrochemical Behavior of a New Titanium Alloy for Dental Applications

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*The aim of this study is to investigate the behaviour of new dental titanium alloys containing either Ta or Mo in Carter-Brugirard on artificial saliva, with and without fluoride ions, and to compare with the behaviour of Ti6Al7Nb alloy, which is used frequently in dentistry. The open circuit potential was measured and the polarization resistance and corrosion currents were estimated from linear sweep voltametric analysis. The results have shown that Ti40Ta and Ti40Mo alloys have a good corrosion resistance in artificial saliva, acidified saliva (pH = 2.5) and fluoridated saliva (1000 ppm F<sup>-</sup> ion). We established that the corrosion of Ti6Al7Nb, Ti40Ta and Ti40Mo alloys is enhanced in fluoridated acidified saliva.*

*Keywords: dental titanium alloys, artificial saliva, Ti40Ta and Ti40Mo alloys*

Titanium and its alloys (specially Ti6Al4V) are widely used in restorative medical surgery such as dental and orthopedic implants, pacemakers and heart valves, because they present high corrosion resistance in physiological media and have a good biocompatibility [1-4]. Their corrosion resistance is due to the spontaneous formation of a superficial oxide film (mainly formed of titanium dioxide TiO<sub>2</sub>) [2], which exhibits high stability in biological fluids. Another interesting property of Ti and its alloys is their high mechanical strength to density ratio. In orthodontics, Ti and Ti6Al4V are usually employed as dental implants [1,6,7] and more recently, as brackets [8].

The Ti6Al4V alloy was the first titanium alloy registered as implant material in the ASTM standards (F-136-84) [9]. The Ti6Al4V and Ti6Al7Nb alloys are among the most commonly used materials, particularly for dental, orthopaedic and osteosynthesis applications [10,11]. Further studies have indicated that vanadium, used to stabilize the  $\beta$ -phase, produces harmful oxides for the human body [10]. The toxicity of vanadium pushed forward the search for materials to replace Ti6Al4V [10]. It has been suggested by Khan et al. [12] that Ti6Al7Nb (now commercially available) can be a better alternative to Ti6Al4V due to its corrosion resistance and resistance to loss of mechanical properties with changes in pH in body fluid environment. Moreover there has been concern, not

yet confirmed, about the association between Al and Alzheimer disease [13,14]. More recently the Ti-Ta alloys were developed [15,17] and expected to become promising candidates for biomedical applications due to their better mechanical bio-compatibility than pure titanium and Ti6Al7Nb alloy.

The aim of this study was to evaluate the simultaneous effect of F<sup>-</sup> ion presence and pH on the electrochemical behaviour of Ti40Ta and Ti40Mo dental alloys in artificial saliva. For comparative purpose, the same measurements were also performed on Ti6Al7Nb alloy.

## Experimental part

### Materials

The origin and chemical composition of the titanium alloys studied are shown in table 1.

The Ti6Al7Nb samples were obtained from a bar stock in annealed state. The Ti40Ta and Ti40Mo alloys were synthesized by the cold crucible levitation melting (CCLM) technique in a CELES induction furnace under a pure Ar atmosphere, which was introduced after several cycles of high vacuum pumping. In order to eliminate the segregation a heat treatment was performed into tubular furnace using the following conditions: (1) homogenization temperature range:  $\beta$ -transus temperature  $\pm 100^\circ\text{C}$ , (2) heating rate,  $5^\circ\text{C}$ , (3) natural cooling. The tests specimens were embedded

**Table 1**  
ORIGIN AND CHEMICAL COMPOSITION OF  
INVESTIGATED TITANIUM ALLOYS

Alloy	Composition (wt %)	Supplier
Ti6Al7Nb	Ti: base, Al: 6, Nb: 7	IMNR, Romania*
Ti40Ta	Ti: 60, Ta: 40	INSA Rennes, France**
Ti40Mo	Ti: 60, Mo: 40	INSA Rennes, France

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in a polytetrafluoroethylene (PTFE) holder specifically designed to connect to a rotating disc electrode (type EDI 101T; Radiometer Analytical). A polymeric resin was used to ensure a tight seal between the alloy specimen and the PTFE holder, as shown in figure 1, to avoid crevice corrosion. Prior to corrosion tests and surface examination, the electrodes were wet-polished with 250, 400, 600, 1000, and 1500 grit metallographic abrasive papers, final polishing was done with 1  $\mu\text{m}$  alumina suspension. The

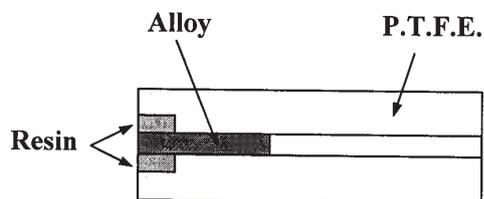


Fig.1. Rotating disk electrode

samples were degreased with ethyl alcohol followed by ultrasonic cleaning with deionised water.

In all measurements the surface area of Ti alloys samples consisting in RDE electrode was 0.21  $\text{cm}^2$ .

#### Tests solutions

Corrosion tests were performed for all the alloys in four different electrolytes:

- the electrolyte reference used was Carter-Brugirard AFNOR/NF (French Association of Normalization) artificial aerated saliva,  $\text{pH} = 8$ . The composition is: NaCl (0.7 g/L), KCl (1.2 g/L),  $\text{Na}_2\text{HPO}_4 \cdot \text{H}_2\text{O}$  (0.26 g/L),  $\text{NaHCO}_3$  (1.5 g/L), KSCN (0.33 g/L), Urea (1.35 g/L). The  $\text{pH}$  measured with a multiparameter analyser CONSORT 831C was 8;

- the second medium was Carter-Brugirard saliva containing lactic acid. This acid was chosen in order to obtain conditions close to the clinical reality because lactic acid is naturally released by bacteria in the oral cavity [18]. The  $\text{pH}$  was fixed arbitrarily at 2.5, knowing that the  $\text{pH}$  of the commercially available fluoridated odontological gels (e.g., Fluogel, Dentoria, Fluocaril, Le Plessis-Robinson, France) is about 4, and that after a meal, the oral cavity  $\text{pH}$  can fall below this value in confined zones [19]. We, therefore, chose the most unfavourable situation;

- the third medium was identical to the reference medium but was enriched with fluoride ions, with a concentration of 0.1% (1 g/L or 1000 ppm), which corresponds to the average fluoride concentration of odontological gels mentioned above. The  $\text{pH}$  was 8;

- the last medium was identical to the second medium, with lactic acid content but enriched with fluoride ions with a concentration of 0.1%, which corresponds to the average fluoride concentration of the odontological gels mentioned above. The  $\text{pH}$  was 2.5.

#### Electrochemical setup

The electrochemical measurements were made with a potentiostatic assembly of three electrodes: a working electrode (rotating electrode), a platinum counter-electrode and a reference electrode of saturated calomel (SCE). The hydrodynamic regime was laminar (criterion  $\text{Re} < 2300$ ) with a rotational velocity at 500 rpm in order to control the mass transfer. A VoltaLab 40 potentiostat controlled by a personal computer with dedicate software (VoltaMaster 4) was used.

For the corrosion tests, first the open circuit potential ( $E_{\text{oc}}$ ) of each specimen was monitored for 24 h after immersion in each electrolyte. This period appeared to be sufficient for the  $E_{\text{oc}}$  to attain steady-state conditions. At the end of open circuit potential test, a linear polarization was performed for each specimen in each electrolyte. Each specimen was polarized from  $-10$  mV to  $+10$  mV referenced to the  $E_{\text{oc}}$  value, at a scanning rate of 0.166 mV/s; estimation of the polarization resistance ( $R_p$ ) was made according to the method described by Mansfeld [20] by using the VoltaMaster 4 software. Finally, potentiodynamic polarization curves were plotted over the potential range of  $-800$  mV to  $+1200$  mV (vs.  $E_{\text{oc}}$ ) at a scanning rate of 0.5 mV/s. Corrosion current density ( $i_{\text{corr}}$ ) and the zero current potential (ZCP) was determined using the curve-fitting routine of the corrosion software.

A coulometric zone analysis was carried out. The method proposed here consists in dividing the polarization curves into two separate zones: zone I, from ZCP up to  $+400$  mV and zone II,  $+400$  mV to  $+700$  mV. The separation is somewhat arbitrary, but the potential domain of zone I, is close to clinical conditions. Although the intensity of the degradation phenomenon may vary from one patient to another, we consider zone I as the high-risk zone and zone II a lower-risk zone barring exceptional situations. The limits of zone I (ZCP to  $+400$  mV) was chosen because it is known that pure titanium in the human body may be exposed to potentials of electrode up to 400 mV [21].

#### Microstructural characterization

The microstructures of the surfaces exposed for electrochemical testing were also studied using an optical microscope (XJP). The microstructures were revealed by etching the sample surface in 10% HF + 5%  $\text{HNO}_3$  solutions for 3-5 s at  $25^\circ\text{C}$ .

#### Result and discussions

When an alloy is placed in the oral environment, an electrochemical interaction (corrosion) takes place. The effect of this interaction may be manifested as: (1) release of soluble metallic ions; (2) retaining of corrosion products on the alloy surface; or (3) a combination of both. These effects, depending on the altered alloy surface and/or the nature of released metallic ions, may trigger adverse biological reactions such as allergy [22].

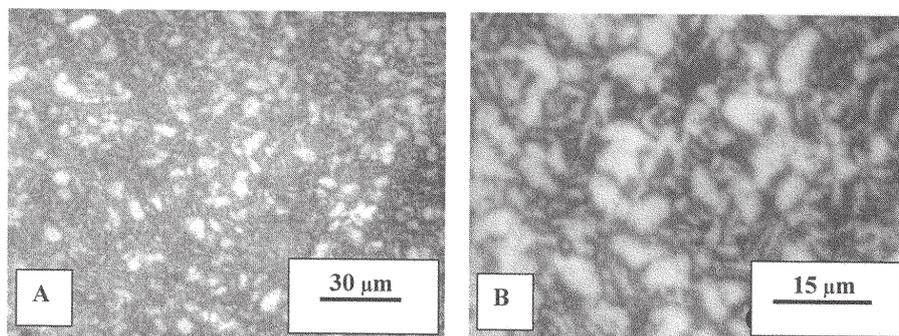


Fig. 2. (A) and (B) Optical micrographs of the surface of Ti6Al7Nb alloy used in the electrochemical study

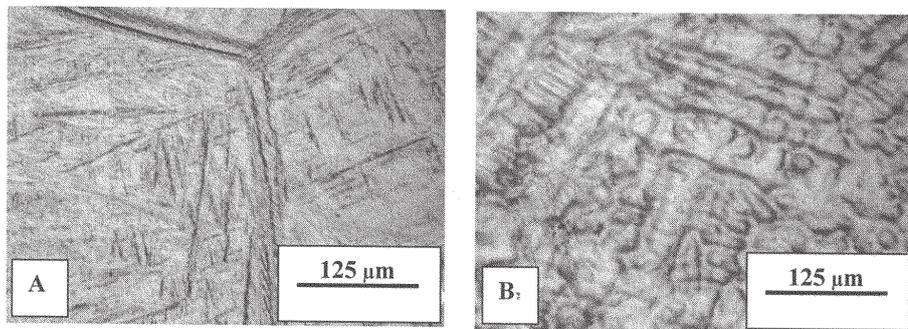


Fig. 3. Optical micrographs of the surface of: (A) Ti40Ta and (B) Ti40Mo alloys used in the electrochemical study

#### Microstructural characterization

The Ti6Al7Nb alloy had a ( $\alpha + \beta$ ) duplex microstructure which consists in a globular and short lamellar  $\alpha$ -phase into  $\beta$ -phase matrix (fig. 2).

The Ti40Ta alloys had also a ( $\alpha + \beta$ ) biphasic structure (fig. 3A). The lamellar  $\alpha$ -phase morphology was observed for Ti40Ta alloy and the surfaces of Ti40Mo alloy showed dendrite microstructure (fig. 3B).

#### Open Circuit Potential, $E_{OC}$ measurements

The open circuit potential of a metal varies as a function of the time but stabilizes at a stationary value after a long period of immersion. This is why our measurements of open circuit potentials are made after 24 h immersion [23].

We noted that the open circuit potential of the Ti6Al7Nb was stabilized at  $-70$  mV in artificial saliva medium (fig. 4). The continued shift in the positive direction of open circuit potential indicated the passivation of the Ti6Al7Nb in this medium [24]. Specimens did not exhibit potential drops associated with surface activation during 24 h exposure in the artificial saliva. This kind of behaviour strongly suggests that the air-formed native oxide on alloys surface is thermodynamically resistant to corrosion in artificial saliva. This hypothesis is confirmed by the Pourbaix diagram of the Ti-H<sub>2</sub>O system [25], where the  $E_{OC}$  value measured after 24 h immersion was reported (see in the followings fig. 7A). In the acidified medium, the shape of the Ti6Al7Nb curve changed very little, suggesting that the material kept its protective passive layer [26]. In the fluoridated medium, the open circuit potential of the Ti6Al7Nb moves towards negative potentials, reaching  $-380$  mV after 24 h. This suggested that the characteristics of passive film changed in this medium, leading to a reduced corrosion resistance. Finally, in the fluoridated acidified saliva, the corrosion potential of the Ti6Al7Nb

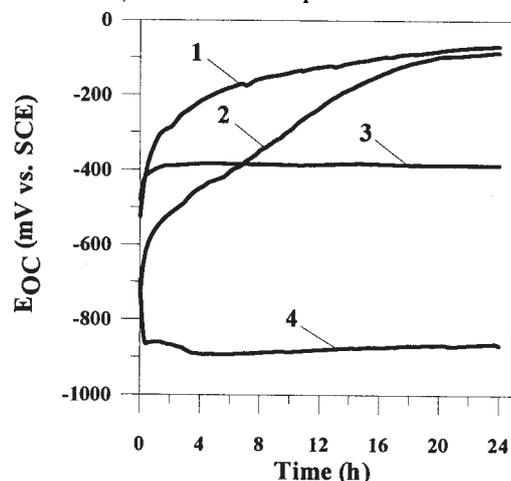


Fig. 4. Open circuit potential evolution against time for Ti6Al7Nb in different media: artificial saliva (curve 1); acidified saliva (curve 2); fluoridated saliva (curve 3) and fluoridated acidified saliva (curve 4)

dropped sharply to a most negative value, of approximately  $-870$  mV, suggesting the complete disappearance of the protective passive layer and a consequently decreasing in the material corrosion resistance [27,28]. All the values are reported in table 2.

The values of  $E_{OC}$  for TiAlNb immersed in artificial saliva, acidified saliva and fluoridated saliva are in the TiO<sub>2</sub> oxide stability region, whereas the  $E_{OC}$  for the acidified fluoridated saliva is in the Ti<sup>2+</sup> ions region.

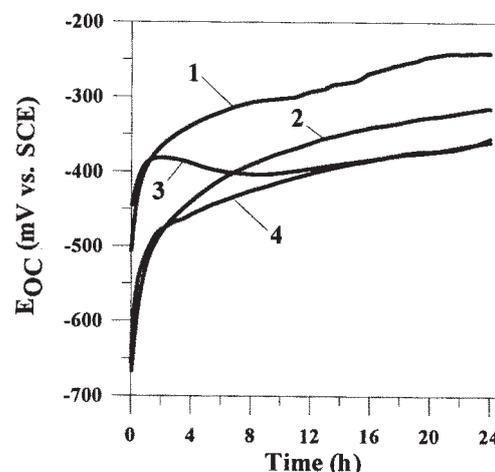


Fig. 5. Open circuit potential evolution against time for Ti40Ta in different saliva media: artificial saliva (curve 1); acidified saliva (curve 2); fluoridated saliva (curve 3) and fluoridated acidified saliva (curve 4)

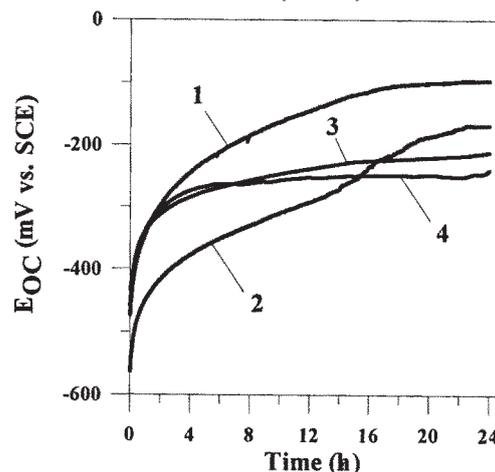


Fig. 6. Open circuit potential evolution against time for Ti40Mo in different saliva media: artificial saliva (curve 1); acidified saliva (curve 2); fluoridated saliva (curve 3) and fluoridated acidified saliva (curve 4)

Figures 5 and 6 present the evolution of the open circuit potential ( $E_{OC}$ ) for Ti40Ta and Ti40Mo alloys as a function of exposure time in all test solutions. For Ti40Ta and Ti40Mo alloys the shapes of the curves in artificial saliva indicated a passive layer formed on the metallic surface.

**Table 2**  
OPEN CIRCUIT POTENTIAL (mV/SCE) OF THE RDE (500 rpm) SAMPLES  
IN DIFFERENT SALIVA MEDIA AFTER 24 h IMMERSION

Open circuit potential, mV vs. SCE ( $E_{OC}$ )	Ti6Al7Nb	Ti40Ta	Ti40Mo
Artificial saliva (pH = 8)	-68	-240	-98
Acidified saliva (pH = 2.5)	-86	-315	-168
Fluoridated saliva (pH = 8)	-386	-355	-211
Fluoridated acidified saliva (pH = 2.5)	-869	-360	-240

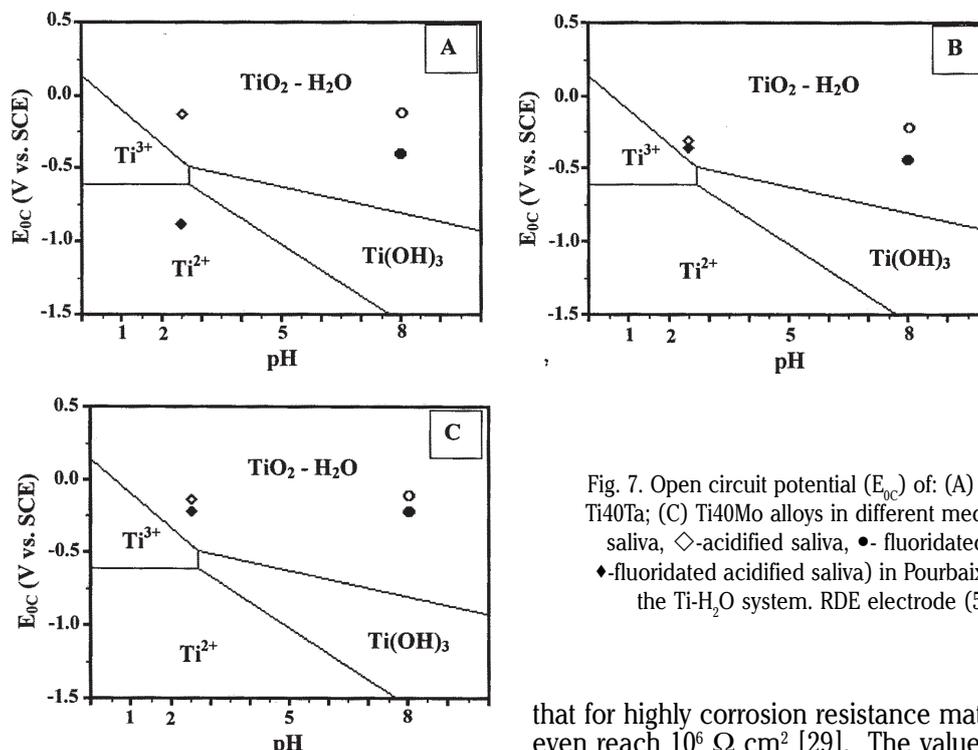


Fig. 7. Open circuit potential ( $E_{OC}$ ) of: (A) Ti6Al7Nb; (B) Ti40Ta; (C) Ti40Mo alloys in different media (o-artificial saliva,  $\diamond$ -acidified saliva,  $\bullet$ - fluoridated saliva and  $\blacklozenge$ -fluoridated acidified saliva) in Pourbaix diagram of the Ti-H<sub>2</sub>O system. RDE electrode (500 rpm)

The  $E_{OC}$  values of Ti40Ta and Ti40Mo alloys measured after 24 h immersion (table 2) are in the stability region of TiO<sub>2</sub> oxide in Ti-H<sub>2</sub>O Pourbaix diagram for all test solutions, suggesting a passive behavior (see also figs. 7B-7C).

*Data obtained from potentiodynamic polarization curves*

While the open circuit potential ( $E_{OC}$ ) provide only qualitative information about the susceptibility to degradation of an alloy surface, polarization resistance ( $R_p$ ) allows a quantitative analysis based on the specific magnitudes of the corrosion rate. It is therefore representative of the degree of protection of the passive layer at the alloy surface.

The polarization resistance ( $R_p$ ) was determined by the tangent of the linear polarization curve ( $\pm 10$  mV vs.  $E_{OC}$  with a 0.166 mV/s scan rate) at  $I = 0$ . Literature shows

that for highly corrosion resistance materials the  $R_p$  may even reach  $10^6 \Omega \text{ cm}^2$  [29]. The values given in table 3 suggested that polarization resistance of all titanium alloys decreased indicating that their corrosion resistance decreased with medium changes in the order: acidified, fluoridated or fluoridated acidified saliva. The polarization resistance values for the Ti40Ta and Ti40Mo alloys were similar to Ti6Al7Nb alloy in different media. Only a substantial difference between  $R_p$  for Ti6Al7Nb alloy and  $R_p$  for Ti40Ta and Ti40Mo alloys in fluoridated acidified saliva was noticed for the last two alloys,  $R_p$  value being much higher.

Plots in a semi-logarithmic coordinates of the polarization curves between -800 mV and +1200 mV vs. SCE for the titanium alloys after 24 h in artificial saliva, acidified saliva, fluoridated saliva and fluoridated acidified saliva are displayed in figures 8-10.

**Table 3**  
POLARIZATION RESISTANCE VALUES ( $k\Omega \text{ cm}^2$ ) OF THE SAMPLES  
IN DIFFERENT SALIVA MEDIA

$R_p$ ( $k\Omega \text{ cm}^2$ )	Ti6Al7Nb	Ti40Ta	Ti40Mo
Artificial saliva	570	570	560
Acidified saliva	560	550	540
Fluoridated saliva	490	430	490
Fluoridated acidified saliva	25	60	65

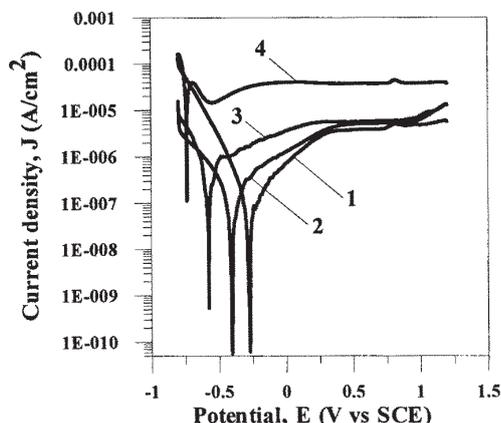


Fig. 8. Potentiodynamic polarization curves for Ti6Al7Nb alloy in different saliva media: artificial saliva (curve 1); acidified saliva (curve 2); fluoridated saliva (curve 3) and fluoridated acidified saliva (curve 4);  $v = 0.5$  mV/s, RDE electrode (500 rpm)

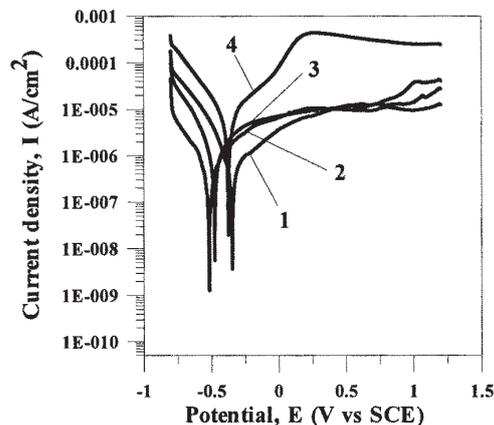


Fig. 10. Potentiodynamic polarization curves for Ti40Mo alloy in different saliva media: artificial saliva (curve 1); acidified saliva (curve 2); fluoridated saliva (curve 3) and fluoridated acidified saliva (curve 4);  $v = 0.5$  mV/s, RDE electrode (500 rpm)

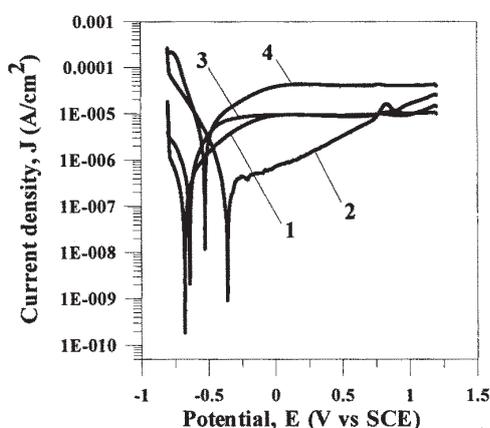


Fig. 9. Potentiodynamic polarization curves for Ti40Ta alloy in different saliva media: artificial saliva (curve 1); acidified saliva (curve 2); fluoridated saliva (curve 3) and fluoridated acidified saliva (curve 4);  $v = 0.5$  mV/s, RDE electrode (500 rpm)

Standard procedures were used to extract “zero current potential” ( $ZCP$ ) and corrosion current ( $I_{corr}$ ) values from the potentiodynamic polarization plots. The average values of  $ZCP$  and  $I_{corr}$  determined by the VoltaMaster 4 program are presented in table 4 and 5.

By comparing with data from table 2, we can notice that in all cases the values determined for the  $ZCP$ , are more negative than those corresponding to  $E_{oc}$ . This variation is probably due to depassivation phenomena on the surface during cathodic scanning.

The values reported in table 5 for all studied titanium alloys suggest that their corrosion resistance decrease with aggressivity of medium in order: acidified, fluoridated or fluoridated acidified saliva. However, the corrosion current

density of Ti40Ta and Ti40Mo alloys as well Ti6Al7Nb alloy in all four-test solutions are comparable.

A distinctive behaviour in the passivation region was observed on the anodic polarization diagrams. The passive current densities obtained in the middle of the passive range of all three titanium alloys in artificial saliva, acidified saliva and fluoridated saliva are of the same order of magnitude ( $1-10 \mu\text{A}/\text{cm}^2$ ), whereas the anodic current densities in fluoridated acidified saliva were around:  $40 \mu\text{A}/\text{cm}^2$  for Ti6Al7Nb and Ti40Ta alloys and  $360 \mu\text{A}/\text{cm}^2$  for Ti40Mo alloy. A decrease in a corrosion resistance and a lower involving of passive oxide film are observed for all the titanium alloys in fluoridated acidified saliva.

Corrosion of titanium alloys is not detected in fluoridated saliva at  $pH = 8$  (after adding  $0.1\%$   $\text{F}^-$  ions,  $1000$  ppm  $\text{F}^-$ ), a fact which indicates the ability of electrodes to grow oxide layers on their surfaces. This suggests that fluoride ions do not hinder the formation of an oxide layer on the electrode surface, as reported by Zwilling et al. [30] who showed that the anodic polarization curve in presence of fluoride in saliva was similar to that in its absence. This can be explained by the competition of the oxide layer formation rate with its removal at the metal/solution interface. The presence of fluoride ions in solution may alter the structure of the oxide layer causing it to be porous [30]. A possible explanation was reported in a previous paper [31] supposing that in the fluoridated acidified saliva a low concentration of fluoride induces the formation of nondissociated  $\text{HF}$  that should dissolve the surface oxide layer by the following reactions [32,33]:



**Table 4**  
ZERO CURRENT POTENTIAL VALUES (mV vs. SCE) OF THE SAMPLES  
IN DIFFERENT SALIVA MEDIA

ZCP (mV vs. SCE)	Ti6Al7Nb	Ti40Ta	Ti40Mo
Artificial saliva	-404	-676	-342
Acidified saliva	-270	-641	-475
Fluoridated saliva	-576	-340	-515
Fluoridated acidified saliva	-749	-527	-376

**Table 5**  
VALUES OF CORROSION CURRENT DENSITIES ( $\mu\text{A}/\text{cm}^2$ ) OF THE  
SAMPLES IN DIFFERENT SALIVA MEDIA

$I_{\text{corr}}$ ( $\mu\text{A}/\text{cm}^2$ )	Ti6Al7Nb	Ti40Ta	Ti40Mo
Artificial saliva	0.5	0.6	0.7
Acidified saliva	0.6	0.7	0.9
Fluoridated saliva	1.1	1.5	1
Fluoridated acidified saliva	39	12	11

**Table 6**  
VALUES OF ELECTRICAL CHARGE CONSUMED DURING THE POLARIZATION CURVES OF THE SAMPLES  
IN DIFFERENT SALIVA MEDIA. ZONE (I): ZCP to +400 mV; ZONE (II): +400 mV to +700 mV

Q ( $\mu\text{C}/\text{cm}^2$ )	Ti6Al7Nb		Ti40Ta		Ti40Mo	
	Zone I	Zone II	Zone I	Zone II	Zone I	Zone II
Artificial saliva	2.5	3	7.5	6.8	6.2	6.6
Acidified saliva	2	2.5	2.4	2.3	5.2	4.8
Fluoridated saliva	6	3.5	8.5	6.8	8.9	6.8
Fluoridated acidified saliva	95	26.5	41	21	189	156

Among the formed titanium fluorides or titanium oxyfluoride, only titanium (IV) fluoride ( $\text{TiF}_4$ ) is a soluble compound [34]. It is suggested that the competition between passive film removal and its formation will be in favor to the latter, with high increase in the positive direction of open circuit potentials. This increase in the open circuit potential to more noble values is attributable to the growth of a barrier film on the metal surfaces.

#### Coulometric analysis

Coulometric analysis provides a simple way for a rough clinical risk analysis. It consists of dividing the anodic polarization curves into two distinct zones: a first zone (I) extending from ZCP to +400 mV and a second zone (II) from +400 mV to +700 mV. For the analysis, the surfaces under polarization curves are integrated for each zone. The result is converted into units of charge ( $\mu\text{C}/\text{cm}^2$ ) by division through the scan rate. The quantities of electrical charge consumed by the corrosion phenomenon by each zone are shown in table 6, showing significant differences between zone (I) and zone (II). The values of electrical charge consumed in zone (I) and zone (II) for titanium alloys in artificial saliva, acidified saliva and fluoridated saliva was low: 1-10  $\mu\text{C}/\text{cm}^2$ . In general the titanium alloys have a much better resistance in artificial and acidified saliva than in fluoridated saliva.

On contrary, the electrical charges for high-risk zone I for titanium alloys immersed in fluoridated acidified saliva was substantial: 40-190  $\mu\text{C}/\text{cm}^2$ . In fluoridated acidified saliva, the titanium alloys have much less corrosion resistance than in other three test solutions.

The results are consistent with the conclusions discussed above from the open-circuit potentials and polarization curves.

#### Conclusion

The corrosion current density of the alloys polarized in Carter-Brugirard artificial saliva, estimated using the Tafel extrapolation method, and provided comparable corrosion currents for Ti40Ta, Ti40Mo and Ti6Al7Nb alloy. The passive behaviour for these alloys is observed in artificial saliva ( $\text{pH} = 8$ ), acidified saliva ( $\text{pH} = 2.5$ ) without  $\text{F}^-$  and for

fluoridated saliva ( $\text{pH} = 8$  and 1000 ppm  $\text{F}^-$ ). A decrease in a corrosion resistance and a lower passive oxide film are observed for all titanium alloys in fluoridated acidified saliva ( $\text{pH} = 2.5$ ). These conclusions are also confirmed by the coulometric analysis. The experimental results confirm the good corrosion resistances of Ti40Ta and Ti40Mo alloys, which are similar to those of Ti6Al7Nb alloy used as standard biomaterial, suggesting their promising potentials for dental applications.

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