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Electrochemical corrosion characteristics of TiTa alloys in commercial mouthwash solution

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Corrosion behaviour of the studied TiTa alloys together with the currently used metallic biomaterials commercial pure titanium (Cp-Ti) was investigated for dental applications. All the samples were examined using electrochemical techniques: open circuit potential, potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS) in two electrochemical media: artificial saliva and in commercial mouthwash solution with 500 ppm F^- (Oral B®, Gillette) at 25°C. The passive behaviour for all the Ti samples is observed for artificial saliva and for commercial mouthwash solution. The TiTa alloys appear to posse's superior corrosion resistance than the Cp-Ti in both electrochemical media.

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Keywords: TiTa samples, Potentiodynamic polarization, Electrochemical impedance spectroscopy

1. Introduction

Titanium and its alloys are one of the most widely studied and used metallic biomaterials. These materials consistently remain the first choice for implants in both medical and dental applications due to their biological advantages and excellent corrosion resistance [1-15].

Ti6Al4V alloy (ASTM F-1472, ASTM F-136, ISO 5832-3) and V free α+β type alloys such as Ti6Al7Nb (ASTM F-1295, ISO 5832-11) and Ti5Al2.5Fe (ISO 5832-10) have been used in dentistry [16, 17]. Further studies have indicated that V, used to stabilize the β-phase, produces harmful oxides for the human body [18, 19]. According to Piazza et al. [20], Al is poorly absorbed within the gastrointestinal tract, very little gets into the blood stream, but has been concerned, not yet confirmed, about the association between Al and Alzheimer disease [21, 22]. In recent years, attempts were made to develop β type titanium alloys with biomechanical compatibility, low modulus and biochemical compatibility [23]. The β-stabilizing elements, such as, Ta, Mo and Sn are selected as safe alloying elements to titanium, which are judged to be non-toxic and non-allergic [24]. Recently investigations [12, 25-27] indicate that the TiTa alloys are expected to become promising candidates for biomedical applications.

Currently, dental gels and rinses containing fluoride are popular for prevention of plaque and caries formation. The presence of fluoride ions in the mouthwash solution brings with it aggressiveness in the attack on titanium. On the other hand, relatively few researches have been carried out to analyze the influence of fluoridated mouthwashes on corrosion resistance of dental alloys [28, 29].

The aim of the present study was to investigate the corrosive effects of fluoridated mouthwash solution on TiTa alloys for dental applications. For comparative purpose, the same electrochemical measurements were also performed on commercial pure titanium (Cp-Ti).

2. Materials and methods

2.1. Materials

The origin and nominal chemical compositions of the titanium samples studied are shown in Table 1.

Table 1. Origin and chemical composition of investigated titanium samples.

Samples	Composition (wt %)	Supplier
Cp-Ti	Ti: 99.9	IMNR, Romania*
Ti30Ta	Ti: 70, Ta: 30	INSA Rennes, France**
Ti40Ta	Ti: 60, Ta: 40	INSA Rennes, France
Ti50Ta	Ti: 50, Ta: 50	INSA Rennes, France

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**INSA Rennes, France

The TiTa alloys were synthesized by cold crucible levitation melting technique in a high frequency induction furnace under a pure Ar atmosphere, which was introduced after several cycles of high vacuum pumping [30]. The Cp-Ti samples were obtained from a bar stock in annealed state. The structural characterization of the Cp-Ti and TiTa alloys was detailed elsewhere [12, 30, 31].

The samples were cut into 0.19 cm^2 sizes and brass nut was attached to sample using conductive paint to ensure electrical conductivity. The assembly was then embedded into an epoxy resin disk. Then the samples were ground with SiC abrasive paper up to 2000 grit, final polishing was done with 1 μm alumina suspension. The samples were degreased with ethyl alcohol followed by ultrasonic cleaning with deionised water and dried under an air stream.

2.2. The electrochemical media

1. Fusayama artificial saliva was selected as it has been shown to produce results that were consistent with the clinical experience of dental alloys [32]. Fusayama artificial saliva [33] was prepared immediately before being used and consisted of: 0.400 g NaCl; 0.400 g KCl; 0.795 g $CaCl_2 \cdot 2H_2O$; 0.780 g $NaH_2PO_4 \cdot 2H_2O$; 0.005 g $Na_2S \cdot 9H_2O$; 1.000g NH_2CONH_2 and distilled water up to 1000 mL. The pH was measured with a multiparameter analyzer Consort 831C. The pH of this saliva corresponding to our first medium was 5.6.

2. The second used medium was Oral B® (Gillette) with 500 ppm F^- ready-to-used mouthwash. The pH of this commercial mouthwash solution corresponding to our second medium was 6.3.

2.3. Electrochemical tests

Electrochemical measurements were carried out in aerated solution at 25 ± 1°C using a Princeton Applied Research potentiostate (Model 263 A) connected with a Princeton Applied Research 5210 lock-in amplifier controlled by a personal computer and a specific software package called Electrochemistry Power Suite (Princeton Applied Research). A glass corrosion cell kit with a platinum counter-electrode and a saturated calomel reference electrode (SCE) were used to perform the electrochemical measurements. All potentials referred to in this article are with respect to SCE.

The following sequence of electrochemical experiments was adopted:

1. Chronoamperometric polarization at –1.5 V for 60 s in artificial saliva;
2. Open circuit potential (OCP) measurement vs. time for 2 hours in artificial saliva (E_1);
3. Electrochemical impedance spectroscopy (EIS) measurement at open circuit potential, E_1, in artificial saliva;
4. OCP measurement vs. time for one hour in mouthwash solution (E_2);
5. EIS measurement at open circuit potential, E_2, in mouthwash solution;
6. Potentiodynamic cathodic polarization from E_1 with 10 x 10^{-3} V/s potential sweep rate;
7. OCP measurement vs. time for one hour in mouthwash solution (E_3);
8. EIS measurement at open circuit potential, E_3, in mouthwash solution;
9. Potentiodynamic anodic polarization from E_3 with 1 x 10^{-3} V/s potential sweep rate;
10. EIS measurement at different imposed potential: 0 V, 0.5 V and 1 V, in mouthwash solution. EIS results at these potentials were obtained 30 minutes after the overpotential has been applied.

The EIS spectra were recorded in the 10^{-2} Hz to 10^5 Hz frequency range. The applied alternating potential signal had amplitude of 10 x 10^{-3} V. In order to supply quantitative support for discussions of these experimental EIS results, an appropriate model (ZSimpWin-PAR, USA) for equivalent circuit (EC) quantification has also been used. For titanium oxide films, a distributed relaxation feature was observed [2]. Due to this fact, in this study a constant phase elements (CPE) was used in the fitting procedure to obtain good agreement between the simulated and experimental data instead of an ideal capacitor. The impedance of the CPE is given by [34]:

$$Q = Z_{CPE} = \frac{1}{C(j\omega)^n}$$

where for n = 1, the Q element reduces to a capacitor with a capacitance C and, for n = 0, to a simple resistor. The n is related to a slope of the Log(Zmod) vs. Log(Frequency) Bode–plots, ω is the angular frequency and j is imaginary number ($j^2 = -1$). The quality of fitting to the EC was judged first by the χ^2 value that was < 5 x 10^{-4} and second by the error distribution versus frequency comparing experimental with simulated data.

2.4. Scanning electron microscopy (SEM) of corroded surfaces

In order to observe the occurrence of the surface effects of the corrosion after anodic polarization treatment, the some corroded surfaces were observed by SEM microscopy. To perform this Vega Tescan scanning electron microscope (model VEGA II LMH) having detector (model xflash, Bruker) for EDX analysis, was used.

3. Results and discussion

The intra-orally temperature widely fluctuates because of ingestion of hot or cold food and beverage. Furthermore, different areas of oral cavity exhibited different temperature. Nevertheless, it can be reasonably approximated in experimental settings if we considered the environmental temperature as 25°C [35].

The open circuit potential (OCP) is the potential at which the material is in equilibrium with the specific environment. In Fig. 1 the variation of OCP with time for all the titanium samples in artificial saliva and in mouthwash solutions is showed.

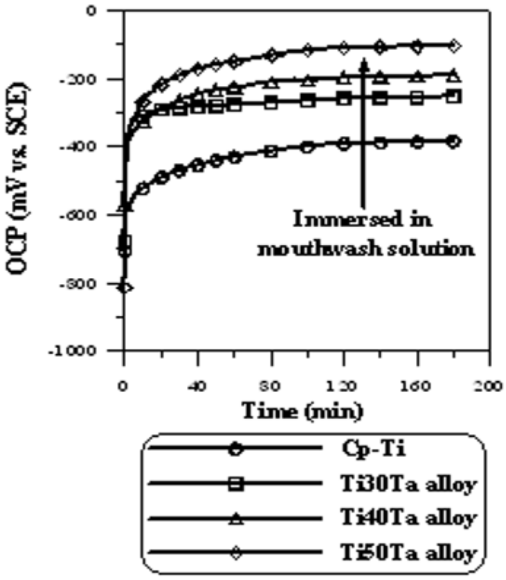

Fig. 1. Variation of open circuit potential (OCP) with time for titanium samples maintained 2 hours in artificial saliva (E_1) and after 1 hour immersed in mouthwash solutions (E_2).

These results are based on the titanium samples studied after 2 hours of immersion in artificial saliva and one hour of immersion in mouthwash solution. Prior to each measurement, the samples were chronoamperometric polarized at –1.5 V in the artificial saliva for 60 s, in order to remove any spontaneously formed surface film [13]. OCP variation is similar for all the titanium samples in both aerated working solution.

From the Fig. 1 all the samples have a tendency to form a passive film by the shift of 1st open circuit potential (E_1) to more positive (noble) direction with respect to time. An abrupt E_1 displacement towards positive potentials was noticed in Fig. 1 during a period of 20 minutes. This initial increase seems to be related to the formation and thickening of the oxide film on the metallic surface. Afterwards, the E_1 increases slowly suggesting the growth of the oxide film. The protecting of the oxide film increased the corrosion resistance. Stable potentials in open circuit measurements is obtained after 40 minutes exposure in artificial saliva, which means the oxide film become stable. 1st open circuit potential (E_1) for TiTa alloys in artificial saliva are more positive than for Cp-Ti, probable due to the positive contribution of the Ta alloying element in the formation of oxide film.

After recorded the 1st open circuit potential (E_1) the samples was immersed in Oral B® mouthwash solution using a second glass corrosion cell. After one hour of immersion in mouthwash solution the 2nd open circuit potential (E_2) don't shows a significant change. Mouthwash solution had no significant influence on the open circuit potential. This behaviour can be essentially attributed to the presence of the oxide film on the Ti samples.

After recorded the 1st and 2nd open circuit potential (E_1 and E_2), the samples was subjected to the cathodic polarization tests. After cathodic polarization, that probably reduces the oxide film, the 3rd open circuit potential (E_3) returns to the same potential range (around to E_2). This behavior suggests that all the titanium samples exhibits a spontaneous passive state and cannot be "activated" by cathodic treatment (Fig. 2).

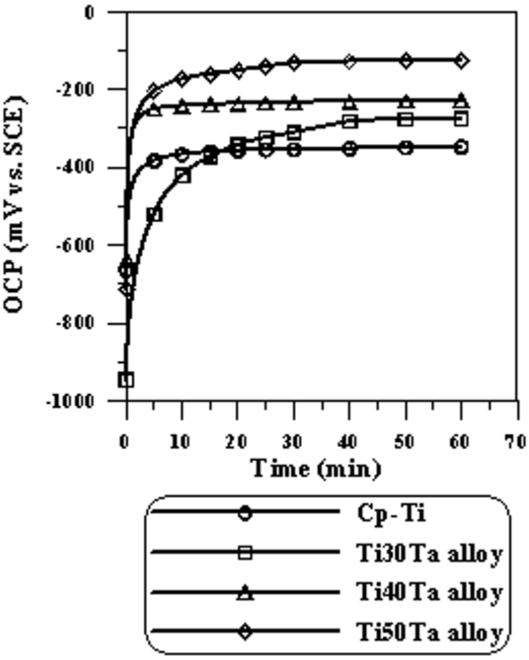

Fig. 2. Variation of open circuit potential (OCP) with time for titanium samples after cathodic polarization and maintained 1 hour in mouthwash solutions (E_3).

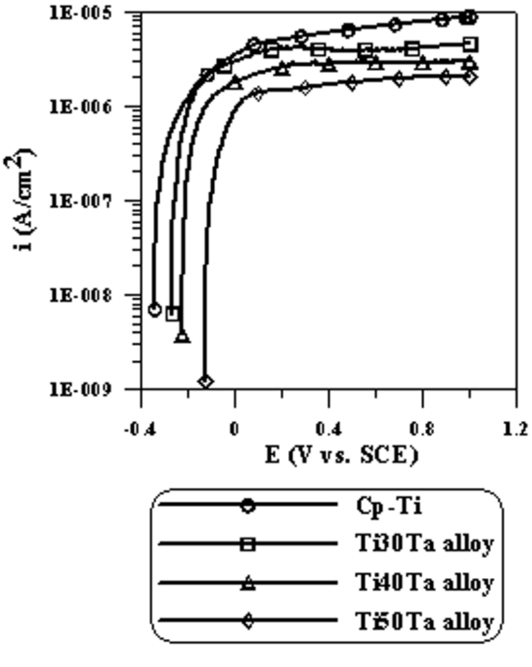

Fig. 3. Potentiodynamic anodic polarisation curves of Ti samples tested in mouthwash solution from E_3 to +1 V.

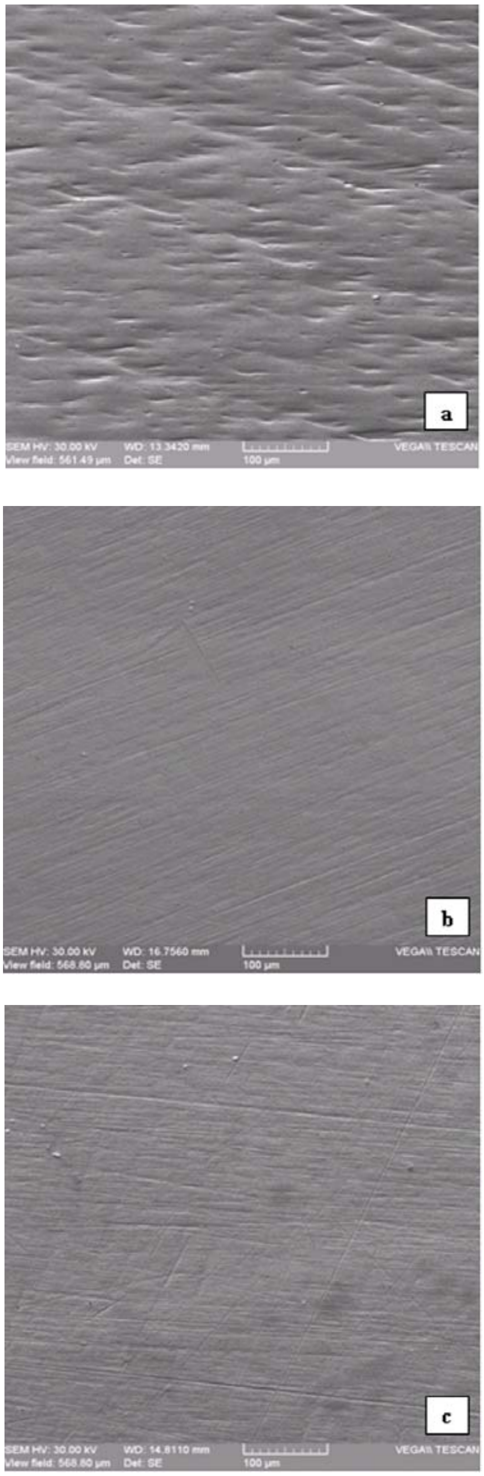

Fig. 4. SEM observations of: (a) Cp-Ti, (b) Ti30Ta and (c) Ti50Ta alloy after anodic polarization tests in mouthwash solution.

Potentiodynamic anodic polarisation curves of Ti samples tested in mouthwash solution from E_3 to +1 V are or displayed in Fig. 3.

All the titanium samples translated directly into a stable passive behaviour from the “Tafel region” without exhibiting a traditional active-passive transition. It can also be seen that the anodic polarization curve of the TiTa alloy shifts to the positive (noble) direction with increasing Ta content. Very low passive current densities (in order of 10^{-6} A/cm^2) were obtained from the anodic polarization curves, indicating a high resistance of all samples in Oral B® mouthwash solution.

Fig. 4 (a-c) shows a typical SEM image of the resulting surface oxide films after anodic polarization in mouthwash solution for Cp-Ti, Ti30Ta and Ti50Ta alloys. A homogeneous oxide layer is developed at the surface of all titanium samples. No pitting or cracks appeared on the alloy surfaces after anodic polarization test.

Fluoride ions can cause localized corrosion and partial dissolution of the passive protective film formed on the titanium samples [36, 37]. In this case the results suggest a non-predominant fluoride effect on the passive behaviours of titanium samples.

Electrochemical impedance spectroscopy (EIS) is a very useful technique for studying the corrosion behaviour of biomaterials. Impedance spectroscopy results for Ti samples in artificial saliva and in mouthwash solution at E_1, E_2 and E_3 potential values are presented as Bode plots (Fig. 5(a-c)).

The phase angle maximum observed for all the samples at E_1 potentials (after 2 hours immersion in artificial saliva) was found to lie in the range of approximately -70° to -80°. The values of the phase angle maximum span three frequency decades (0.1 Hz to 100 Hz), gradually decreases with decreasing frequency (below 0.1 Hz). High impedance values (order of 10^6 Ω cm^2) were obtained from medium to low frequencies for TiTa alloys at E_1, suggesting, high corrosion resistance in artificial saliva.

For the interpretation of the electrochemical behaviour of a system from EIS spectra, an appropriate physical model of the processes occurring on the electrode (equivalent circuit) is necessary. Fitting of the impedance was done with an equivalent circuit (EC) using a series combination of the solution resistance, R_{sol} (around 100 Ω cm^2), with two RQ elements in parallel: $R_{sol}(R_{oL}(Q_{oL}(R_{bL}Q_{bL})))$. The quality of the EIS data fitting estimated by both the values of chi-square (χ^2) test (between 5×10^{-4} and 10^{-5}) and the comparison of the error distribution vs. frequency (± 2% for whole frequency range) corresponding experimental and simulated data.

The EC presented in Fig. 6a is based on a model used by Pan et al. [2] to simulated data in saline solution. These authors viewed the surface layer formed on titanium as a two-layer oxide, with an inner barrier layer and an outer porous layer. Studies performed on Ti based alloys under physiological conditions showed that the EC proposed by Pan et al. [2] can be used successfully to describe the behaviour of these materials as well [3, 11, 14, 38-40]. The high-frequency parameters R_{oL} and Q_{oL} represent the properties of the reactions at the outer porous passive film/solution interface. The parameter R_{bL} coupled with Q_{bL} describes the processes at the inner barrier layer at the electrolyte/compact passive film interface. The values of fitted parameters of the EC are presented in Table 2.

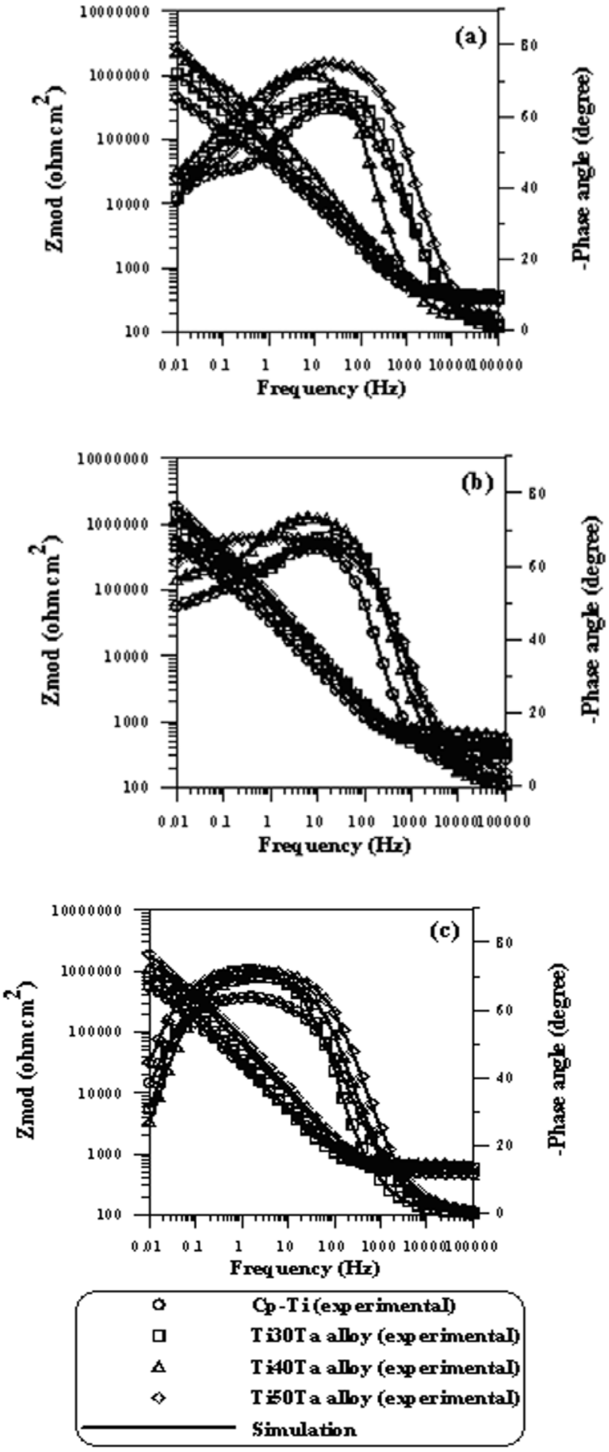

Fig. 5. Bode plots recorded for at selected potentials: (a) E_1, (b) E_2 and (c) E_3 in artificial saliva and mouthwash solution, at 25°C.

In the Fig. 5(a-c), the experimental data are shown as individual points, while the theoretical spectra resulted from the fits with a relevant EC model are shown as lines. High values of R_{bL} (order of 10^6 Ω cm^2) are observed at E_1 potentials for all the TiTa alloys, confirming the formation of a compact layer with high corrosion protection ability. R_{bL} was greater than R_{oL} by a factor of nearly 10^2 (Table 2) showing that the resistance of the oxide film on the all the sample and at E_1 potentials is due to this layer. High impedance values (order of 10^6 Ω cm^2) were obtained for TiTa alloys at E_2, after one hour immersion in mouthwash solution. All these samples in mouthwash solution over a relatively wide-frequency region display a capacitive behaviour typical of passive system. Again, the values of the phase angle maximum span three frequency decades (0.1 Hz to 100 Hz).

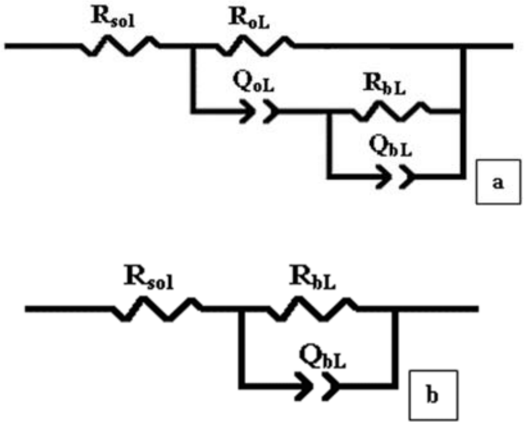

Fig. 6. Equivalent circuits (EC) used to fit the impedance data.

Table 2. Values of fitted parameters of the equivalent circuits as function of selected potential Ti samples in artificial saliva and mouthwash solution

Sample code	Potential	Q_{oL}, μS cm^{-2} s^n	n_{oL}	R_{oL}, kΩ cm^2	Q_{bL}, μS cm^{-2} s^n	n_{bL}	R_{bL}, MΩ cm^2
Cp-Ti	E_1 E_2 E_3	14 12 -	0.85 0.85 -	31 150 -	11 11 11	0.80 0.82 0.80	0.5 0.5 0.4
Ti30Ta	E_1 E_2 E_3	14 12 -	0.83 0.84 -	35 168 -	9.9 9.8 9.9	0.83 0.85 0.84	1.3 1.2 1.1
Ti40Ta	E_1 E_2 E_3	14 12 -	0.82 0.83 -	31 175 -	9.7 9.8 9.8	0.85 0.84 0.85	2.1 1.9 1.8
Ti50Ta	E_1 E_2 E_3	13 11 -	0.85 0.86 -	45 214 -	- 9.7 9.8	- 0.85 0.85	2.3 2.2 2.1

The EIS spectra were fitted and the model $R_{sol}(R_{oL}(Q_{oL}(R_{bL}Q_{bL})))$ was proposed for E_2. The values of R_{bL} remain around 10^6 Ω cm^2, for all the TiTa alloys, at E_2 potentials, indicating high corrosion resistance after one hour of immersion in mouthwash solution. The R_{oL} increases around 10^5 Ω cm^2, for all the samples, at E_2 potentials. It is also observed that the n_{bL} values corresponding to E_2 were found around 0.85. This indicated that the compact passive film exhibits a near capacitive behaviour.

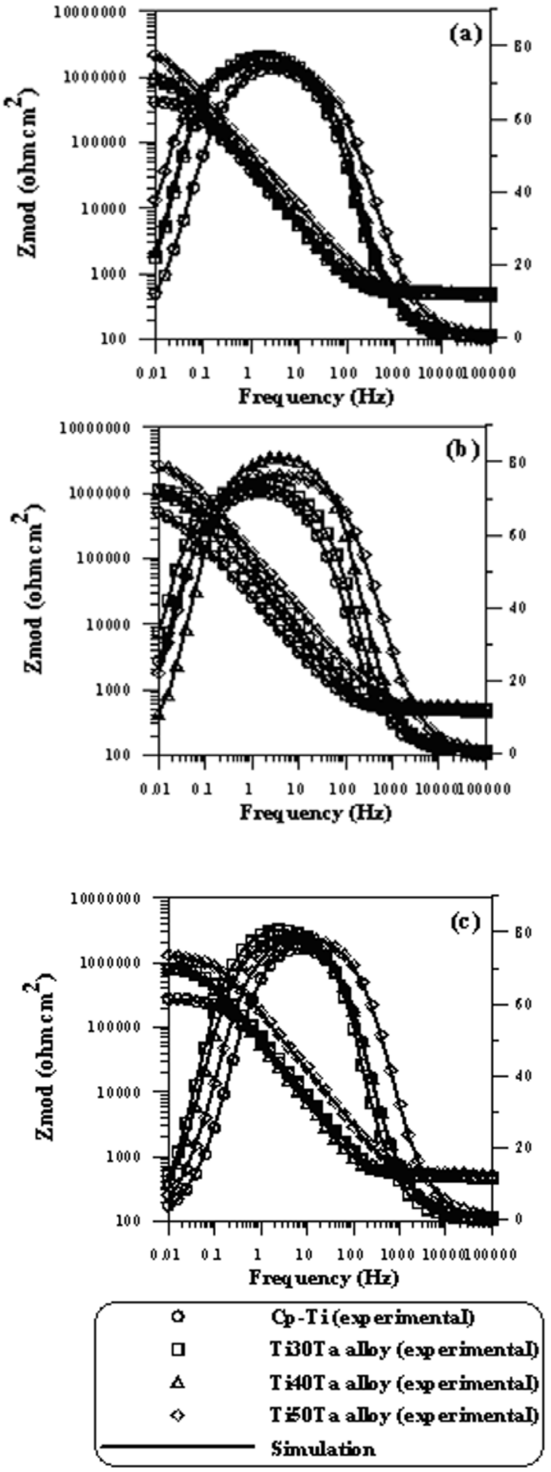

Fig. 7. Bode plots recorded for at selected potentials: (a) 0 V, (b) 0.5 V and (c) 1 V in mouthwash solution, at 25^oC.

In case of titanium samples at E_3 potentials the Bode-phase plots are in agreement with an EC with one time constant. The EC (Fig. 6b) is characterized by one parallel combination terms ($R_{bL}Q_{bL}$) in series with the resistance of the solution (R_{sol}). Gonzalez and Mirza Rosca [3] proposed $R_{sol}(R_{bL}Q_{bL})$ as the EC model to fit the EIS data in the case of the single passive oxide film present on the metal surface. This simple EC has been generally used successfully to describe the behaviour of titanium alloys in different solutions [12, 41]. The chi-square value (χ^2) between 6 x 10^{-4} and 10^{-5} and error distribution vs. frequency values (± 2%) points to excellent agreement between the experimental and simulated values. The values of the parameters (R_{bL}, Q_{bL}) obtained with the fitting procedure are reported in Table 2. The higher R_{bL} of TiTa alloys at E_1, E_2 and E_3 potentials indicates that these alloys possesses a superior corrosion resistance than Cp-Ti in artificial saliva, and in mouthwash solution.

Fig. 7(a-c) showed the EIS spectra, in the form of Bode plot, of titanium samples in mouthwash solution, at 0 V, 0.5 V and 1 V. EIS results at different potentials were obtained 30 minutes after the overpotential has been applied. The impedance data obtained at various potentials (0 V, 0.5 V and 1 V) were compared in order to evaluate the influence of the potential on the passive oxide characteristics.

The EIS measurements at 0 V, 0.5 V and 1 V shows single-time constant confirming the presence of a single layer on the surface of the titanium samples in mouthwash solution. In order to quantitatively evaluate the corrosion resistance from the impedance data, the experimental curves were fitted using the $R_{sol}(R_{bL}Q_{bL})$ model (Fig. 6b).

Again, the chi-square value (χ^2) between 5 x 10^{-4} and 10^{-5} points to excellent agreement between the experimental data and simulated values. The values of the parameters (R_{bL}, Q_{bL}) obtained with the fitting procedure are reported in Table 3.

Table 3. Values of fitted parameters of the equivalent circuits as function of selected potential Ti samples in mouthwash solution

Sample code	Imposed potential, V	Q_{bL}, μS cm^{-2} s^n	n_{bL}	R_{bL}, MΩ cm^2
Cp-Ti	0	11	0.83	0.4
	0.5	11	0.83	0.5
	1	12	0.85	0.3
Ti30Ta	0	9.9	0.85	1.1
	0.5	9.8	0.86	1.3
	1	9.9	0.86	1.1
Ti40Ta	0	9.8	0.85	1.3
	0.5	9.8	0.85	1.5
	1	9.9	0.85	1.2
Ti50Ta	0	9.8	0.85	1.9
	0.5	9.7	0.85	2.2
	1	9.8	0.86	1.8

As the potential changes from 0 V to 0.5 V, R_{bL} increases. These results seem to correspond to a thickening of the titanium passive film. As the potential increases from 0.5 V to 1 V the R_{bL} decreases slowly. The decrease in resistance indicates that the oxide layer may become more defective at large over potential [11, 39]. But the R_{bL}, of all the samples, in mouthwash solution was large at

1 V (order of 10^6 Ω cm^2) as seen in Table 3. For highly corrosion resistance materials [42] the polarization resistance (R_p) may even reach 1 MΩ cm^2. This indicates that the samples are still highly resistant to corrosion even at large over potentials. TiTa alloys and Cp-Ti were shown to be passive in mouthwash solution.

In terms of EIS analysis, the corrosion resistance of titanium samples immersed in mouthwash solution is improved with addition of Ta. The additions of the Ta have a positive contribution in the formation of the passive oxide film. This was probable, attributed to the enrichment of Ti surface with elemental Ta and oxidized Ta_2O_5 which is more stable than TiO_2 [43], but the nature of the oxide film was not investigated in this study. It is noteworthy that the volume fractions of β-phase increases along with the increase of alloy Ta content. The decrease of α-phase proportion leads to improvement the corrosion resistance of the Ti alloys.

4. Conclusions

On the basis of the above discussion, the main conclusions can be summarized as such:

The passive behaviour for all the titanium samples is observed for artificial saliva and for Oral B® (Gillette) commercial mouthwash solution.

Over the frequency range applied the equivalent circuit (EC) employed for the description of the Ti samples provides the best fitting of the experimental data. The EIS results of the samples in artificial saliva can be fitted using the model of $R_{sol}(R_{oL}(Q_{oL}(R_{bL}Q_{bL})))$ and in commercial mouthwash solution can be fitted using the model of $R_{sol}(R_{bL}Q_{bL})$. These results confirming the presence of a two layer film consisting of an inner barrier responsible for the corrosion protection, and an outer porous layer on the surface of the samples in artificial saliva and a single layer (barrier) on the surface of the samples in commercial mouthwash solution.

Values of barrier layer indicate that the Ta used as alloying element improve the electrochemical corrosion behaviour of TiTa alloys in both electrochemical media, compared to the Cp-Ti.

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