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Corrosion resistance of titanium alloys in the artificial saliva solution

J. Loch [a,*], H. Krawiec [a], A. Łukaszczyk [a], J. Augustyn-Pieniążek [b]

[a] Department of Chemistry and Corrosion of Metals, Faculty of Foundry Engineering, AGH University of Science and Technology, ul. Reymonta 23, 30-059 Krakow, Poland

[b] Department of Physical and Powder Metallurgy, Faculty of Metals Engineering and Industrial Computer Science, AGH University of Science and Technology, Al. Mickiewicza 30, 30-059 Krakow, Poland

* Corresponding e-mail address: beazurek@pg.gda.pl

ABSTRACT

Purpose: The purpose of this article was to characterize the corrosion behaviour and compare two biomedical titanium alloys (Ti-6Al-4V and Ti-10Mo-4Zr) in an artificial saliva solution (MAS) containing lactic acid and hydrogen peroxide (H_2O_2) used in dentistry. The addition of these two compounds simulate the situation, where the alloy is implanted in the human body and hydrogen peroxide is generated by the inflammatory reaction and lactic acid is release by bacterial in the oral cavity.

Design/methodology/approach: In this studies were used following electrochemical techniques: Open Circuit Potential (OCP), Linear Sweep Voltamperometry (LSV), Chronoamperometry at constant potential and Electrochemical Impedance Spectroscopy (EIS). Electrochemical impedance spectra were carried out at the 0.5 V vs. Ag/AgCl potential. The EIS data were fitted using the ZViev software.

Findings: The results presented in the work demonstrate that the titanium alloys have a good corrosion resistance. The corrosion behaviour was determined by surface condition of alloys and presence different chemical compounds in the solution. For Ti-10Mo-4Zr titanium alloy in MAS with different concentration of hydrogen peroxide in anodic domain it was seen more clearly.

Research limitations/implications: In the future passive films of both titanium alloys will be investigated by: X-ray photoelectron spectroscopy (XPS) and scanning electron spectroscopy (SEM).

Originality/value: The corrosion behaviour of biomedical titanium alloy contains molybdenum and zirconium selected as safe alloying elements for human body is presented and compared to commercial Ti-6Al-4V alloy. The corrosion resistance of the titanium alloys was investigated in the artificial saliva solution with addition of lactic acid and hydrogen peroxide.

Keywords: Biomaterials engineering; Titanium alloys; Corrosion resistance; Lactic acid; Fluoride ions; Hydrogen peroxide

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PROPERTIES

1. Introduction

Titanium and its alloys are the most attractive metallic materials used in dentistry, because of their good biocompatibility, light weight, excellent corrosion resistance, and high strength [1-2]. Compared with other metallic biomaterials, such as Co–Cr alloys and stainless steels, the Ti alloys possess lower modulus, superior biocompatibility and enhanced corrosion resistance. These attractive performances promote the development and application of new orthopaedic Ti alloys in the medical field [3]. Before the widespread application of titanium biomaterials, stainless steel and Co–Cr–Mo alloy were often used as a bio-implants, but some problems such as Ni-toxicity, corrosion degradation and others made it crucial to develop alternative biomaterials [4]. Moreover, Ti-based alloys have been proposed to prepare wires or lingual arches in orthodontic patients who are allergic to the nickel present for example in nitinol (NiTi) [5] or other alloys. The biocompatibility of titanium implant is determined by the chemical properties of the oxide layer. The passive layer plays an important role for the surrounding it tissues, and the passive film cannot undergo break down if the implant is to be successful [6].

The oral environment undergoes the significant changes during the day. The mastication forces, oral pH, the presence of different chemical compounds from the food, drinking water, mouthwash products and inflammatory reactions play an important role on the degradation of the implants. Lactic acid is naturally released by bacteria in the oral cavity. This acid simulates the conditions which are reached during drinking acidic beverages, regurgitation or the presence of dentobacterial plaque. Bacteria present in the dental plaque generate a formation of mixture of acids like lactic, acetic and other metabolic acids which cause the decrease of pH up to 4 or lower. Such low pH of the saliva destroys the tooth [2-3].

It has been shown that the hydrogen peroxide (H_2O_2) is produced by bacteria and leukocytes during inflammatory response and it attacks the surface of Ti alloys [5]. Additionally, the unexpectedly high in vivo oxidation/corrosion rates of titanium sometimes was found, as an effect of generation of H_2O_2 in the biological system during implantation [7-8]. Hydrogen peroxide generates oxidation and hydroxylation of the titanium surface by removing the native oxide layer, stripping away organic contaminants and producing a purified and disinfected final product [9]. Application of bioactive coatings on the surface of alloys and thermo-chemical treatment based hydrogen peroxide is very important for medical implants. This modify the surface chemistry and topography of titanium alloys surface for obtaining a bioactive behaviour [10]. Furthermore, the oxides formed at the presence of H_2O_2 are rougher and display higher ionic conductivity than the oxide formed in the absence of peroxide [6]. The formation of the thick and rough oxide layer on the metal surface releases of titanium ions to the solution [11].

The new generation of titanium base alloys for implant applications must satisfy many concerns. The most important alloys include non-toxic elements for body fluids. The new titanium alloys which are consider as non-toxic alloys contain as a alloying elements molybdenum and zirconium. In the previous works the corrosion behaviour of these alloys have been studied in Ringer and Hank's solution [12-17].

In this paper, the corrosion behaviour of Ti-10Mo-4Zr is compared to Ti-6Al-4V alloy in artificial saliva solution at 37°C. The aim of this study was to investigate the corrosion resistance of both titanium alloys in the artificial saliva containing the lactic acid and hydrogen peroxide.

2. Experimental

Experiments were performed on titanium alloys Ti-6Al-4V and Ti-10Mo-4Zr. In order to increase the grain size, the first alloy (Ti-6Al-4V) was heated at 740°C for 70 minutes. Ti-6Al-4V alloy is composed to two metallic phases: α and β phase. Second alloy Ti-10Mo-4Zr is only composed to β-phase. Specimens of Ti alloys were mechanically ground via a standard procedure using wet silicon carbide papers of decreasing grit (500, 1200, 2400, 4000) and then smoothed using diamond suspensions (down to 1 μm). Between each step, specimens were ultrasonically cleaned in ethanol for 5 minutes.

All electrochemical tests were conducted using a potentiostat PGSTAT302N AUTOLAB potentiostat/galvanostat. Electrochemical measurements were carried out at the global scale, in aerated solutions. A classical three-electrode cell was used with a silver/silver chloride electrode (3 M KCl) as reference electrode and a platinum plate as counter electrode.

Corrosion tests were performed in a simulated body fluid: Mayer artificial saliva solution (MAS) at 37°C. Chemical composition of MAS was presented in Table 1.

Experimental measurements were performed adding to MAS solution the following chemical compounds: lactic acid and hydrogen peroxide in different concentration (Table 2). Oral bacteria metabolization imitate addition of lactic acid (80%, Avantor Performance Materials) to artificial saliva solution. The inflammatory conditions after implantation was simulated through the addition of H_2O_2 (30%, Avantor Performance Materials).

Table 1.
Chemical compound of Mayer artificial saliva solution (MAS); pH=6.6

Chemical compound,	NaCl	KCl	$CaCl_2$	$NaH_2PO_4*2H_2O$	KSCN	$Na_2S * 9H_2O$	Urea
g/l	0.4	0.4	0.6	0.26	0.3	0.005	1.0

Table 2.
Artificial saliva solution (MAS) with added different chemical compounds

Indication of solution	Added chemical compound	Content, unit/l	pH of solution
MAS + lactic acid	80% lactic acid solution – $C_2H_4OHCOOH$	To pH	4.0
MAS + 1 H_2O_2	30% hydrogen peroxide solution – H_2O_2	1.0 ml	4.3
MAS + 10 H_2O_2	30% hydrogen peroxide solution – H_2O_2	10.0 ml	4.5

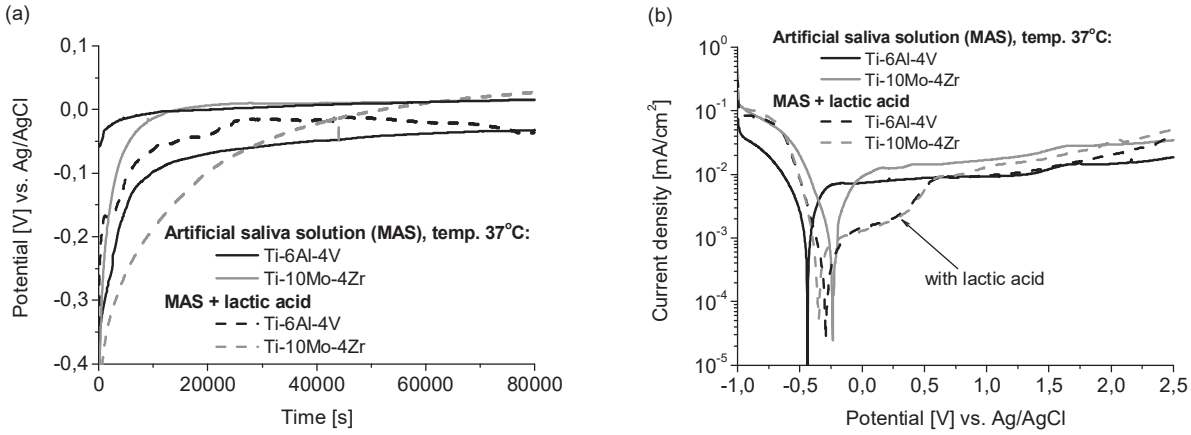

Fig. 1. Electrochemical behaviour of Ti-6Al-4V and Ti-10Mo-4Zr alloys in artificial saliva solution (MAS) with lactic acid (pH = 4.0), at 37°C: (a) evolution of the corrosion potential vs. time and (b) polarization curves at 1 mV/s

Such concentrations are likely to be generated in the body in case of inflammation in the surrounding of implant or present in mouth washes or in fluorination preparations.

Potentiodynamic polarization scans were plotted at a scan rate of 1 mV/s from -1 V vs. Ag/AgCl (3 M KCl) up to 2.5 V vs. Ag/AgCl (3 M KCl). Electrochemical impedance spectroscopy (EIS) diagrams were plotted on the two alloys within a frequency range of 100 kHz to a few mHz (70 points) using 10 mV peak-to-peak sinusoidal potential difference. EIS measurements were performed after 1200 s of immersion at various applied potentials 0.5 V vs. Ag/AgCl (3 M KCl). Interpretations of the spectra were performed utilizing the ZViev program. The impedance data and fitted data were interpreted in Bode amplitude and phase angle plots.

3. Results and discussion

3.1. Influence of lactic acid

Open circuit potential measurements (Fig. 1a) and linear polarisation (Fig. 1b) were used to demonstrate the differences in corrosion behaviour of Ti-6Al-4V and Ti-10Mo-4Zr alloys in artificial saliva solution (MAS) with or without lactic acid. The OCP curves of both alloys take on an upward trend and they obtain gradually the stable value in MAS and in solution with lactic acid. During the initial stabilisation period of 20000 s after the immersion, similar trends were observed on both materials in MAS, but in MAS with lactic acid the stable value of OCP was obtained over 70000 seconds. In MAS, as shown in Fig. 1b, both titanium alloys showed typical passive behaviour, with the current density maintained at 12-22 $\mu A/cm^2$ in the passive range. Only the polarisation curves plotted for both Ti alloys in MAS with lactic acid exhibit the lower current density in the potential range between -0.25 V and 0.70 V vs. Ag/AgCl, Fig. 1b. The greater current density in the cathodic domain is observed for acidic solution. This is the region in which the hydrogen reduction and evolution of hydrogen gas occur (reaction 2). In order to maintain a balance of charge, two reactions occur at the surface of titanium alloys. The metal dissolution reaction, or anodic reaction, results in the loss of electrons (for titanium and other alloying elements), while the coupled cathodic reaction results in a species gaining electrons.

An example of these two reactions is shown in Equations (1) and (2), where metal is being oxidized to ions while hydrogen ions are being reduced such that hydrogen is evolved (especially after addition of lactic acid) [17]:

$$M \rightarrow M^{n+} + ne \quad (1)$$

$$2H^{+} + 2e \rightarrow H_2 \uparrow \quad (2)$$

3.2. Influence of hydrogen peroxide

The presence of hydrogen peroxide in artificial saliva solution (MAS) shifts the OCP potential to positive direction at two H_2O_2 concentrations and two pH values for both titanium alloys (Fig. 2). The values of OCP measured for titanium alloys immersed in MAS for 24 h was shown in Table 3. The highest potential exhibited Ti-6Al-4V and Ti-10Mo-4Zr alloys in solution with 1 ml H_2O_2 (MAS + 1 H_2O_2). The potential of surface for titanium alloys in this measurements was found to increase with the order: MAS < MAS+10 H_2O_2 < MAS+1 H_2O_2. Potential increase in MAS with H_2O_2 is associated with enhance rate growth of oxide film. Karthega et all sugared that especially growth of globular particles over entire surface [18].

Table 3.
OCP for Ti-6Al-4V and Ti-10Mo-4Zr alloys after 24 h immersion in MAS with hydrogen peroxide in different concentration

Potential [mV vs. Ag/AgCl] in:	MAS	MAS + 1 H_2O_2	MAS + 10 H_2O_2
Ti-6Al-4V	-23	137	96
Ti-10Mo-4Zr	-38	99	58

Corrosion resistance of titanium alloys is determined mainly by the chemical composition of alloys, dissolution of alloying elements, formation titanium oxide (TiO_2) and catalysed decomposition of the peroxide [11]. Pan et all sugared that the inner layer (untreated alloys) is compact and similar stoichiometric to TiO_2. While outer layer (film on the surface) is porous, nonstoichiometric and rich in hydroxylated compounds. Schematic growth of the oxide film on the titanium in solution with hydrogen peroxide shows Fig. 3 [7].

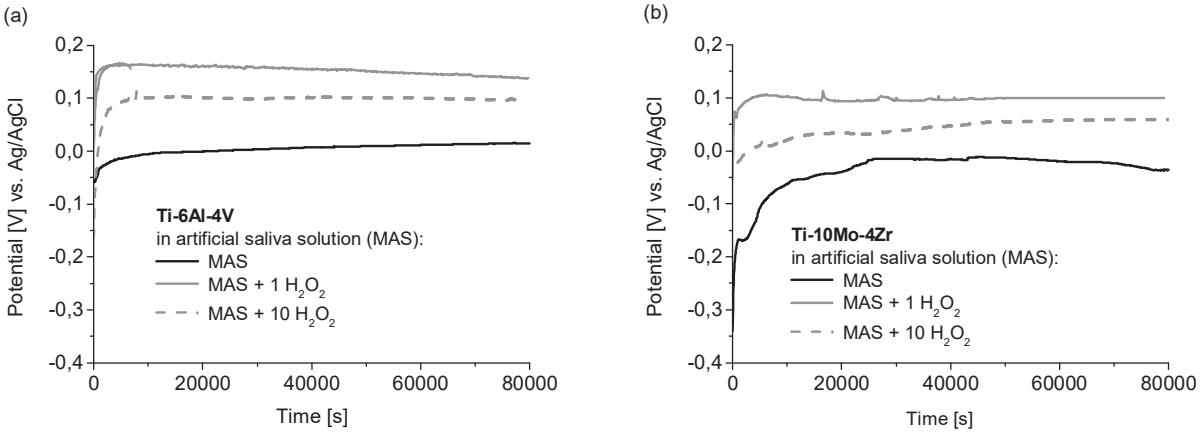

Fig. 2. Electrochemical behaviour: evolution of the corrosion potential vs. time of (a) Ti-6Al-4V and (b) Ti-10Mo-4Zr alloy in artificial saliva solution (MAS), MAS+1 H_2O_2 and MAS+10 H_2O_2, at 37°C

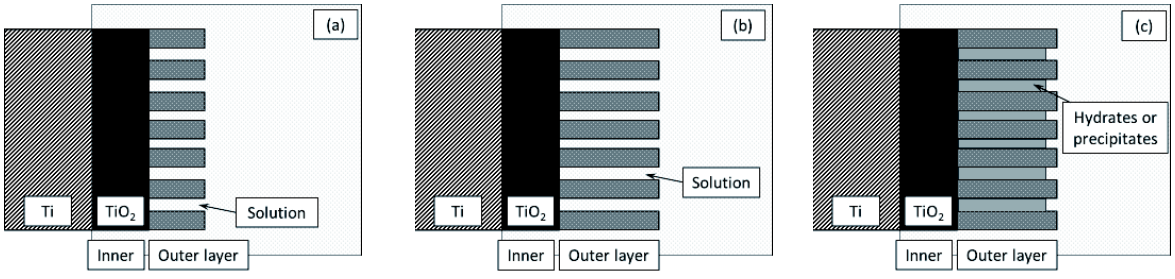

Fig. 3. Schematic representation of the oxide film formed on titanium exposed in the PBS (Phosphate Buffered Solution): (a) without H_2O_2, (b) with H_2O_2, earlier stage, (c) with H_2O_2, later stage [7]

On the surface of titanium alloys two phenomena will take place in contact with H_2O_2: (3) the Ti-catalysed decomposition of hydrogen peroxide and the corrosion of the metal [10]. The H_2O_2 decomposes to oxygen and water at the Ti surface. This can be illustrated by the following equations [6]:

$$2TiO_2 + H_2O_2 + 2e = Ti_2O_3 + H_2O + O_2 \quad (3)$$

$$Ti_2O_3 + H_2O_2 = 2TiO_2 + H_2O + 2e \quad (4)$$

The influence of concentration of hydrogen peroxide on the corrosion behaviour of Ti-10Mo-4Zr and Ti-6Al-4V was then investigated in artificial saliva solution with H_2O_2 at 37°C. The potentiodynamic polarization curves for Ti-6Al-4V and Ti-10Mo-4Zr in MAS with different concentration of H_2O_2 are presented in Fig. 4a,b. For both titanium alloys the equilibrium potential is lower in MAS without H_2O_2. Additionally, the presence of H_2O_2 shifts the equilibrium potential to more noble potential values for Ti alloys. In the cathodic domain current density for titanium alloys in MAS with H_2O_2 compare to MAS is greater, especially in the solution containing 1 ml of hydrogen peroxide. The current density measured in the anodic branch of both alloys in MAS with 1 ml of H_2O_2 is greater than the current registered in the neutral solution. The current density in MAS+10 H_2O_2 is similar to the current measured in MAS. Therefore, the two alloys are less resistant to corrosion in less concentration H_2O_2. For example, in the case of Ti-10Mo-4Zr, the current density at 0.5 V vs. Ag/AgCl is roughly 18.8 $\mu A/cm^2$ for MAS+1H_2O_2 and 8-14 $\mu A/cm^2$ for MAS and MAS+10H_2O_2.

Differences in corrosion behaviour result from chemical properties of the titanium oxide TiO_2 which is the main oxide present in the passive film. As it was stated before the presence of H_2O_2 in the solution significantly changes the properties of the structure of the oxide layer formed on the surface of Ti alloys. Therefore, to confirm these changes the electrochemical impedance spectroscopy (EIS) measurements were performed in the anodic domain in MAS containing H_2O_2.

Evolution of current density vs. time during chrono-amperometry test of both titanium alloys shows Fig. 5. The time required to obtain the stable value of current density was 1200 s for both alloys in MAS and MAS with added hydrogen peroxide. Current density is around $1.3*10^{-3}$-$4.3*10^{-4}$ mA/cm^2.

Figure 6a shows the impedance spectra (Nyquist plot) obtained for both titanium alloys at potentials of 0.5 V vs. Ag/AgCl (potential in the passive range). In order to obtain the steady state first the chronoamperometry at potential 0.5 V vs. Ag/AgCl was performed for 1200 seconds, than the EIS spectra were plotted at this potential. Figure 6b,c shows EIS spectra presented as Bode plot in of the both titanium alloys in MAS and MAS+10H_2O_2.

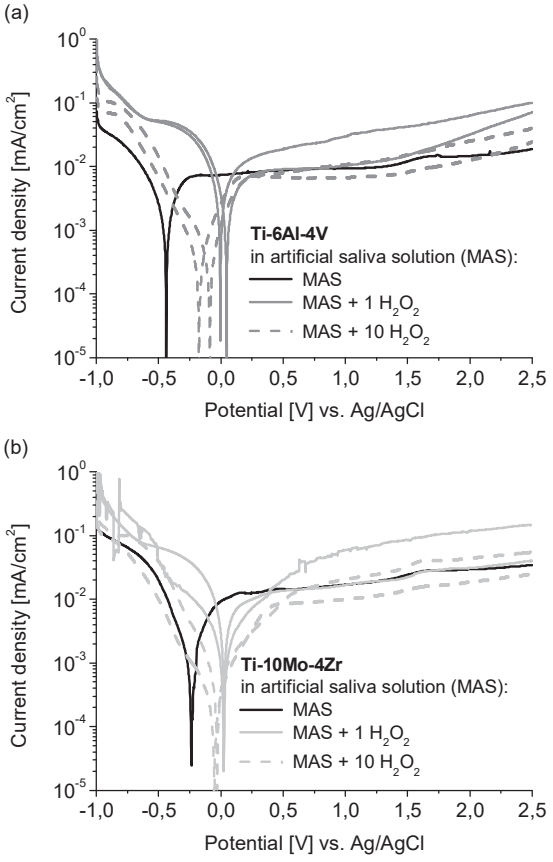

Fig. 4. Electrochemical behaviour: polarization curves at 1 mV/s of (a) Ti-6Al-4V and (b) Ti-10Mo-4Zr alloy in artificial saliva solution (MAS), MAS+1 H_2O_2 and MAS+10 H_2O_2, at 37°C

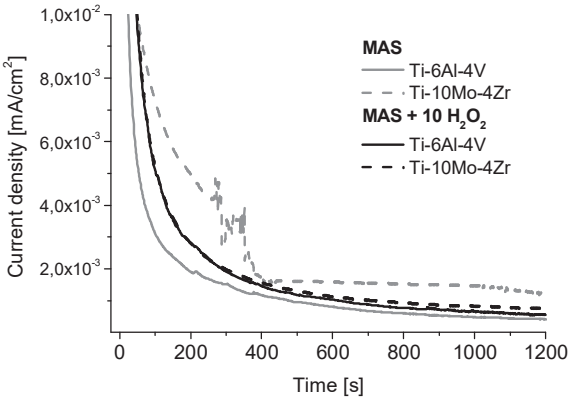

Fig. 5. Evolution of the current density vs. time during global tests of Ti-6Al-4V and Ti-10Mo-4Zr alloys, in artificial saliva solution (MAS) and MAS+10 H_2O_2, at 37°C at 0.5 V vs. Ag/AgCl

From Fig. 6c, higher Z moduls at lower frequency in the Bode impedance plot indicated a better corrosion resistance of both titanium alloys in MAS with H_2O_2.

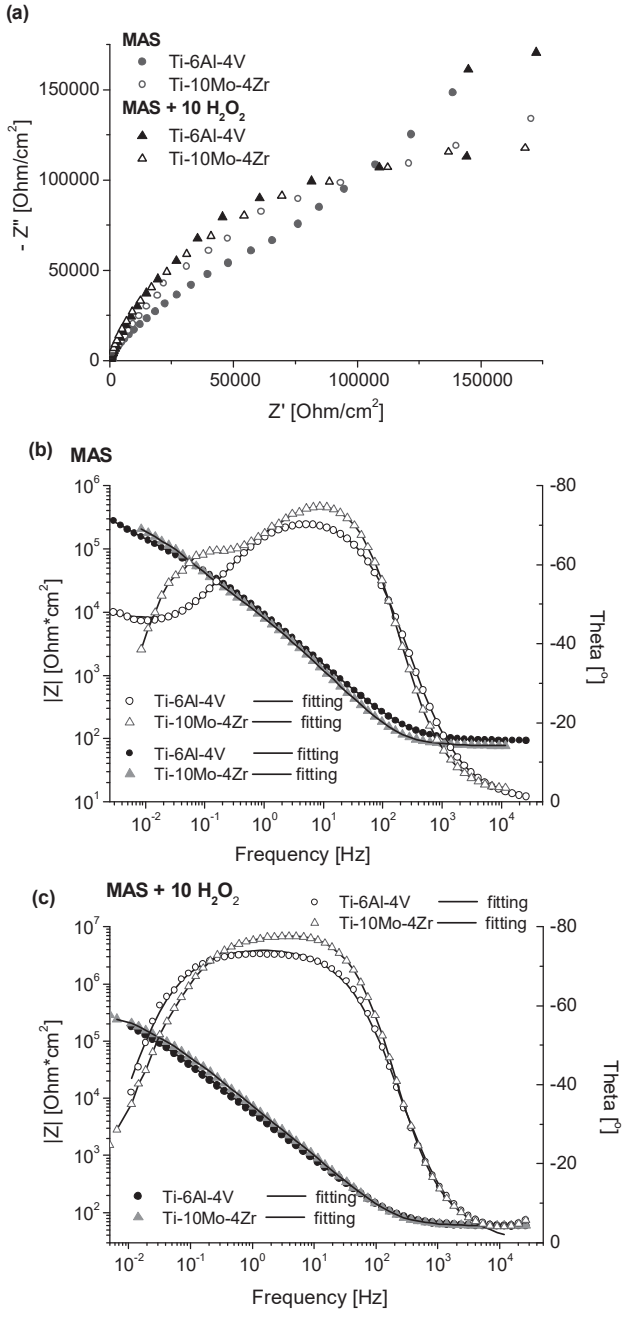

Fig. 6. Electrochemical impedance diagrams: (a) Nyquist plot, (b-c) Bode plots obtained on the Ti-6Al-4V and Ti-10Mo-4Zr alloys in (b) MAS and (c) MAS+10H_2O_2 at 37°C at 0.5 V vs. Ag/AgCl. Potential was applied 1200 s before EIS measurements

The equivalent circuit as shown in Fig. 7a was used to fit the EIS data. The equivalent circuit consisted of the electrolyte resistance (R1), the coating resistance (R2) and constant phase elements (CPE). The fitted equivalent circuit model (Fig. 7a) clearly indicated the presence of the passive oxide layer over the surface of Ti-alloys. Equivalent circuit modified by an additional Warburg resistance (W) was used for fitting of EIS spectra obtain for Ti-6Al-4V alloy in MAS (Fig. 7b). Warburg resistance at low frequency range, corresponding to the effect of concentration polarization dominated by diffusion on the electrode reaction [19]. Warburg-type diffusion component in the EIS spectrum that can be attributed to diffusion processes taking place in the solid phase. This suggests the presence of pores in the outer part of the passive film with diffusion effects inside them [20].

The spectra obtained for Ti-10Mo-4Zr alloy in MAS was fitted using the circuit model represented as R1(R2CPE1)(R3CPE2) (Fig. 7c). It indicated the formation of inner barrier layer and outer porous gel layer. This type of circuit can be considered as an electrical representation of a two layers model of the oxide film, consisting of an inner barrier and outer porous layer [18,21].

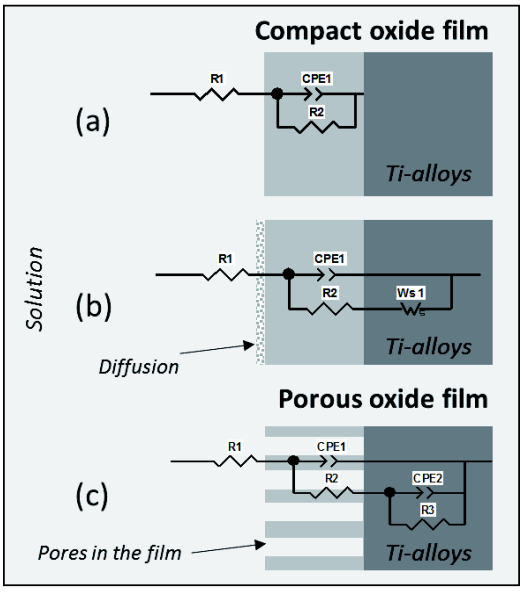

Fig. 7. Equivalent circuits used for fitting EIS data of investigation samples. On the basis of [22]

Table 4 shows that the resistance (R2) of the outer porous layer is smaller than the resistance (R3) of the inner barrier layer. The outer porous layer contributes less to the protection effect of the coating. The inner barrier layer plays an important role in inhibiting the penetration of the ions in the electrolyte [19].

Table 4.
Numerical data derived from fitting EIS spectra

	Sample	R1, $\Omega*cm^2$	CPE1-T, $Fs^{n-1}*cm^2$	CPE1-P	R2, $\Omega*cm^2$	Ws1-R, $\Omega*cm^2$	Ws1-T	Ws1-P
MAS	Ti-6Al-4V	92.3	$2.2*10^{-5}$	0.83	61416	$6.9*10^{5}$	301.3	0.52
	Sample	**R1, Ω*cm]**	**CPE1-T, $Fs^{n-1}*cm^2$**	**CPE1-P**	**R2, $\Omega*cm^2$**	**CPE2-T, $Fs^{n-1}*cm^2$**	**CPE2-P**	**R3, $\Omega*cm^2$**
	Ti-10Mo-4Zr	77.0	$2.0*10^{-5}$	0.89	24517	$1.89*10^{-5}$	0.75	337370
MAS + 10H_2O_2	Ti-6Al-4V	58.3	$3.7*10^{-5}$	0.84	301540	-	-	-
	Ti-10Mo-4Zr	58.0	$2.7*10^{-5}$	0.88	270350	-	-	-

The passive film formed at 0.5 V vs. Ag/AgCl on the Ti-alloys has capacitive character. The values of CPE1-P for both alloys is around 0.86. It can be seen that the values of R2 in MAS with H_2O_2 is very high around $2.7\text{-}3.0*10^5$ $\Omega*cm^2$ for both alloy, significantly higher compared to MAS.

A compact or a porous oxide film on titanium alloys can be represented by three different equivalent electrical circuits from fitting of EIS spectra. The study indicates that the addition of hydrogen peroxide to artificial saliva has an slightly beneficial effect on corrosion resistance of Ti-alloys. EIS studies show that the resistance and the structure of the passive film formed on Ti-alloys depend on the chemical composition of alloy and environment especially of the presence of oxidizing agents.

4. Conclusions

This study reports the corrosion behaviour of two titanium alloys using electrochemical tests in artificial saliva solution (MAS) at 37°C. Under the experimental conditions of this study, the following conclusions can be drawn:

1) The results presented in the work demonstrate that titanium alloys: Ti-6Al-4V and Ti-10Mo-4Zr have a very good corrosion resistance in MAS.
2) The presence of lactic acid in artificial saliva solution has little impact on corrosion behaviour of both titanium alloys, visible in the cathodic domain. The current density increase because pH of solution is lower.
3) In H_2O_2 free MAS, titanium forms a passive film with high corrosion resistance. H_2O_2 addition in MAS results in an enhanced growth rate of the oxide film with titanium and can lead to decrease or increase corrosion resistance.
4) The electrochemical studies revealed that titanium alloys in MAS + 10 H_2O_2 possessed low current density in anodic domain and excellent corrosion resistance compared to MAS and MAS + 1 H_2O_2.
5) The EIS spectra suggested, that corrosion resistance of titanium alloys is determined by structure of passive film and chemical compounds of solution.
6) The experimental results confirm that the corrosion resistance of the studied new titanium Ti-10Mo-4Zr alloy is similar to that of commercial Ti–6Al-4V alloy currently used as biomaterial, suggesting their potential for dental applications.

Acknowledgements

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