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CORROSION REACTIVITY IN THE PRE-CLINICAL STUDY OF 316L AND 321 STAINLESS STEEL FOR DENTISTRY APPLICATIONS

Now, the use of any medical device based on metals or alloys, especially intended for dentistry applications, is impossible without preclinical evaluation of its anticorrosion properties. Today, the use of stainless steels with AISI standardization, with predilection 316L and 321, are preferred for ergonomic reasons due to their high operational reliability and optimal mechanical properties for functionality over time. In this regard, 316L and 321 stainless steels are tested for comparison in the solution that simulates human saliva with different pH. Stainless steel samples were subjected to corrosion in Fusayama-Meyer and Carter-Brugirard saliva. In-situ electrochemical measurements were applied, such as the open circuit potential (OCP) and electrochemical impedance spectroscopy (EIS). The results show that the corrosion resistance of 316L is superior to 321 in saliva solution at both pH values.

Keyword: Corrosion; electrochemical methods; stainless steel; human saliva

1. Introduction

The most used stainless steels in the dental field is the austenitic series 300, namely for the manufacture of stamped crowns, the base of dental bridges, crochet hooks for orthodontic appliances [1]. Among the austenitic with considered biological in oral health, 316L and in a small part, 321 can provide excellent corrosion resistance, with optimal mechanical properties, as well as the availability of financially point of view [2-4]. However, they have a disadvantage, characterized by the toxic effects of corrosion products (trace elements of chromium, copper, iron, nickel, etc.) that enter the saliva and then involuntarily assimilated by the human body.

316L stainless steel with a subsequent content of 2% molybdenum, determines a film of denser chromium oxide, which increases passivity in chlorides and marine environments, with improved resistance to corrosion in points (pitting) and crevices [3,5]. In the case of austenitic stainless steel AISI 321 stabilized with elementary particles of titanium (a derivative of AISI 304) takes place in the preferential formation of titanium carbon precipitates (TiC), thus keeping chromium in solution for protection against corrosion [6].

The widespread use of metals and alloys in dentistry is due to their high resistance to wear and relatively low biological activities. However, there is a problem in the use of metallic materials that requires increased attention not only in medicine but also in other industries. One of the main factors that reduces the reliability and strength of the metal product is corrosion.

The dangerous consequences of corrosion include the loss of important technological properties such as mechanical strength, ductility, hardness and others [7].

Metal prostheses and metal fillings in some patients can cause the development of a complex of pathological symptoms, which is often referred to as the universal term "intolerance to metal inclusions in the oral cavity." This complex of symptoms is based on the processes of electrochemical corrosion of the metals and alloys in the oral cavity. Electrochemical corrosion in the oral cavity begins when electrical potentials occur between different metal inclusions or between prostheses and the oral fluid, which is an electrolyte. The atoms of a more negative electrode migrate in the form of positively charged ions in the electrolyte, which causes various pathological phenomena, for example, galvanizes [6,8-9].

It is known that the more negative the electrode potential is, the more pronounced the tendency of the metal to dissolve into electrolytes. Therefore, the measurement of electrochemical potentials is the most important task in terms of predicting the intensity of the electrochemical corrosion process of dental

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devices in the oral cavity [10]. In recent years, scientists have paid attention to the study of electrochemical corrosion of dental alloys, especially alloys based on metals [9,11-13]. It was found that the kinetics of electrochemical reactions depends significantly not only on the material of the electrode, but also the physical-chemical properties of its surface [8,10,14-15].

Analysis of data from the literature has shown that different types of mechanical processing or exposure to active chemical environments used in dental prosthesis technology can lead to specific changes in the physical-chemical structure of the thin oxide layer on the surface, causing, in particular, a complex symptom of intolerance to metal alloys. Such changes can affect the structure of the native oxide layers and the corrosion behavior of the basic metal alloys and, therefore, their biocompatibility and various pathological manifestations. The structural and chemical state of the surface is what determines the mechanism and kinetics of surface processes [15-16]. The influence of fluoride ions coming from toothpaste during the hygiene of the oral cavity is also studied because the metallic structures are affected [4,17-19].

This preclinical experimental study aims to compare the reactivity at the level of anticorrosive properties of 316L and 321 stainless steels in biological solutions of human saliva type with different pH, such as Fusayama Meyer and Carter Brugirard saliva.

2. Experiment

Austenitic stainless steel plates with a thickness of 1.5 mm, both for AISI samples 316L and 321 were delivered by Direct Line Inox, where they were subsequently sectioned into segments with standard dimensions of 25 mm × 25 mm. The contact with the electrical source of the samples was made by copper wire with Ø 2.5 mm and insulated with epoxy resin, to delimit the default-working surface to 225 mm^2. The nominal composition of the austenitic stainless steels in the given study is presented in Table 1.

TABLE 1

Chemical composition of AISI 316L and AISI 321 stainless steels

Element / wt%	C	Mn	Si	Ti	Mo	Ni	Cr	Fe
SS AISI 316L	≤0.03	≤2	1	—	2.0-2.5	11-14	16.5-18.5	Bal.
SS AISI 321	0.08	2	1	0.48	—	10.5	18	Bal.

The 316L and 321 stainless steel samples were tested using electrochemical methods in Fusayama-Meyer saliva (SFM) and Carter-Brugirard saliva (SCB). Both solutions are based on the chemical composition and physical-chemical characteristics (determined with the CONSORT C-533 multiparameter analysis device) according to Table 2.

To evaluate and compare the anticorrosive properties of the 316L and 321 stainless steel samples, an electrochemical

TABLE 2

Chemical composition of biological solutions Fusayama Meyer saliva and Carter Brugirard saliva

Nr. Crt.	Chemical compound	Fusayama Meyer saliva [g / L]	Carter Brugirard saliva [g / L]
1	NaCl	0.4	0.7
2	KCl	0.4	1.2
3	$CaCl_2$	0.8	—
4	NaH_2PO_4*12H_2O	0.79	—
5	Na_2HPO_4*7 H_2O	—	0.26
6	$NaHCO_3$	—	1.5
7	CH_4N_2O	1	1.3
8	KSCN	—	0.33
9	Purified water (H_2O)	Balance	Balance
	pH Conductivity [mS/cm] Salinity [ppt]	5.7 2.5 1.3	8.1 5.3 2.8

cell with 150 mL of saliva solution is used, Fig. 1, in which the working electrode (WE) represents one of the studied sample, the reference electrode (RE) being Ag / AgCl (E = +199 mV vs NHE) saturated with potassium chloride (KCl), and in the case of the auxiliary electrode a platinum mesh (Pt) is used. The primary data collection and analysis is performed with the Voltalab PGZ100 electrochemical workstation, and the raw results were purchased and processed with –Voltamaster 4 software.

The applied electrochemical methods used to determine the corrosion behavior of these two stainless steel tested in saliva solutions with different pH are: open circuit potential during 12 hours with meas period 0.2 sec and electrochemical impedance spectroscopy initiated from 100 kHz to 1 mHz with a sinusoidal amplitude of 10 mV and 20 frequency per decade.

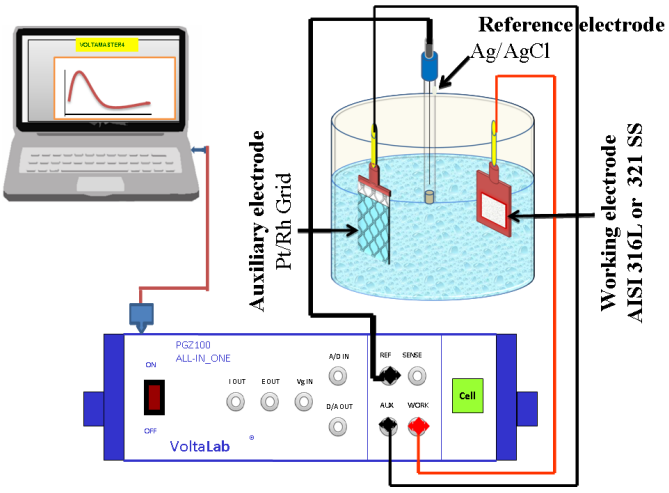

Fig. 1. Experimental set-up for comparative preclinical electrochemical corrosion investigation of AISI 316L si AISI 321 in saliva solutions

For the accuracy and precision of the experimental data and last but not least the need for repeatability of the tests per-

formed, the 316L and 321 stainless steel samples were subjected to a protocol for preparing and cleaning the work surface with alcohol, distilled water and drying.

3. Results and discussion

3.1. Open circuit potential (OCP)

According to a predetermined protocol, the evolution of the open circuit potential versus time is the first set method. Open circuit potential method evaluates the behavior of the material to corrosion response in time as a the qualitative evaluation, showing the tendency of the material oxidation in the respective solution towards an active state of corrosion (dissolution) or passive state of better corrosion resistance.

In Fig. 2 it can be observed the evolution of the open circuit potentials for 316L and 321 samples immersed in Fusayama Meyer saliva (pH value of 5.7) during 12 hours. Each measurement was repeated three times on the same type of steel to verify the reproducibility of the results.

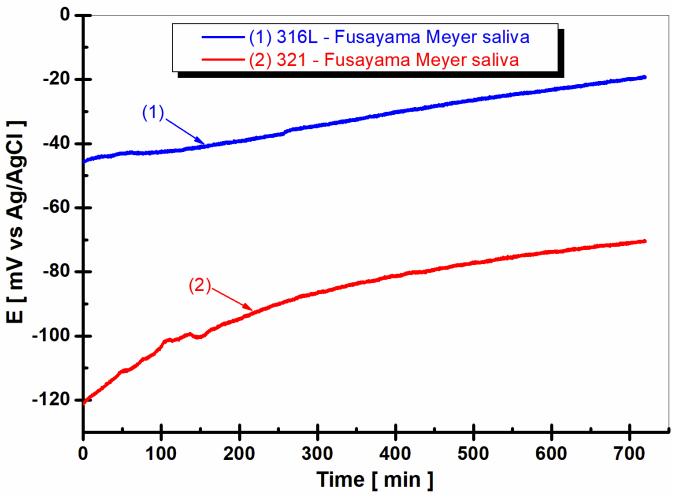

Fig. 2. Evolution of free potential (OCP) in biological Fusayama Meyer saliva solution for: (1) 316 L stainless steel; (2) 321 stainless steel

As shown in Fig. 2, curves (1), the free potential of 316L stainless steel has more positive (nobler) values than the free potential of 321 stainless steel immersed in Fusayama Meyer saliva. The open circuit potential starts at E = –45.5 mV vs Ag/AgCl at the moment of immersion having a slight tendency to move also towards more positive values (nobler) during the 12 hours of monitoring.

At the end of monitoring the free potential of this stainless steel reach a value of E = –19.4 mV vs. Ag/AgCl. This behavior shows that the surface of 316L stainless steel manages to passivate in the Fusayama Meyer saliva solution.

The open circuit potential of 321 stainless steel, Fig 2, curve (2), starts from an E = 120.4 mV vs. Ag/AgCl having the same tendency to move towards more positive (nobler) values during the 12 hours of monitoring in Fusayama Meyer saliva. At the end, the open circuit potential reaches the value of E = –70.5 mV vs. Ag/AgCl, being always more negative as compared with the value of open circuit potential of 316L stainless steel in the same saliva solution.

The free potential evolution for both studied stainless steels in Carter Brugirard saliva with pH 8.1 is shown in Fig. 3.

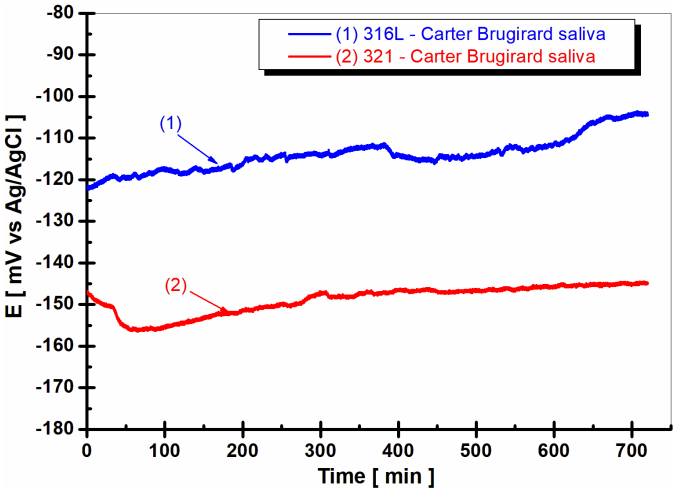

Fig. 3. Evolution of free potential (OCP) in biological Carter Brugirard saliva solution for: (1) 316 L stainless steel; (2) 321 stainless steel

As a comparison of Fig. 2 and Fig 3 it can be observed that both stainless steels studied show much more negative free potential values in Carter Brugirard saliva as compared with Fusayama Meyer saliva. This behavior can be attributed to the fact that saliva Fusayama Meyer has a weak acidic pH, which makes, in a short period of time, to form an oxide layer on the surface of the samples. The low alkaline pH of Carter Brugirard saliva makes the passive oxide film unstable because this type of chromium oxide can be dissolved in alkaline solutions.

Thus the value of the open circuit potential of 316L stainless steel, Fig. 3, curve (1), starts from the value E = –122.1 mV vs. Ag / AgCl with a slight tendency to move towards more positive values during the 12 hours. At the end of the 12 hours the value of the free potential reaches the value of E = –104.5 mV vs. Ag / AgCl which is 85.1 mV more negative (more active) than the free potential value recorded for the same stainless steel in Fusayama Meyer saliva.

The value of open circuit potential of 321 stainless steel in Carter Brugirard saliva is also located in this saliva at more negative values than the values recorded for 316L stainless steel in the same saliva. Thus the free potential starts from E = –147.31 mV vs. Ag / AgCl, with a slight tendency to move towards more negative (more active) values during the first hour of monitoring and then to follow the same tendency of a slight shift towards more positive (more noble) values. At the end of the 12 hours of monitoring the open circuit potential for this steel in Carter Brugirard saliva is with 74.37 mV more negative (more active) than the free potential value recorded by the same steel in Fusayama Meyer saliva.

For both stainless steels, the values of the free potential recorded in Carter Brugirard saliva are more negative than the values recorded in Fusayama Meyer saliva. This behavior can be attributed to the fact that passivable alloys containing chromium form a thin layer of chromium oxide that dissolves rapidly in alkaline solutions.

From the results of the open circuit potential, it can be conclude that 321 stainless steel present more negative values of the free potential in both saliva solutions used than the 316L steel.

The tendency of open circuit potential for a material to move towards more negative values means that the material is not capable to form a protective oxide layer leading to a lower corrosion resistance of the material in the respective environment.

3.2. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy is the most powerful technique for characterizing the surface of materials in relation to their specific environment of use [4,18,20-21].

Electrochemical impedance results for a solid electrode / electrolyte interface often reveal a frequency dispersion that cannot be described by simple electrical equivalent circuit elements such as resistances, capacitances, inductances, or convective diffusion (e.g., Warburg impedance). Frequency dispersion is generally attributed to a "capacity dispersion", expressed in terms of a constant phase element (CPE) [22-25]. Different equations have been proposed in the literature [22].

The evolution of the stainless steel interface shown in Figs. 4 and 5 as a Nyquist representation is characterized by a behavior with constant phase element (CPE).

Thus this behavior can be better quantified by graphical representation of the imaginary part of the impedance versus frequency, in logarithmic coordinates [22,23] as shown in Figs. 6 and 7.

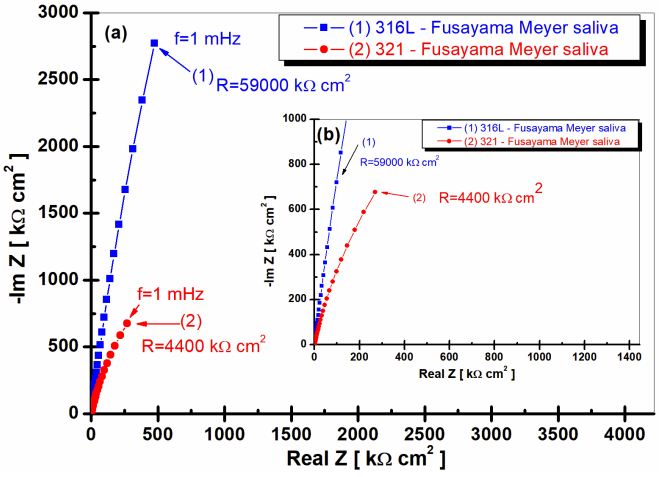

Fig. 4. (a) Nyquist drawing of electrochemical impedance spectroscopy results recorded and fitted in Fusayama Meyer saliva solution for: (1) 316 L stainless steel; (2) 321 stainless steel. Symbols are experimental results while the line represents the fitted curve. (b) Zoom in the high frequency domain of diagram (a) to see better the differences between the two stainless steels

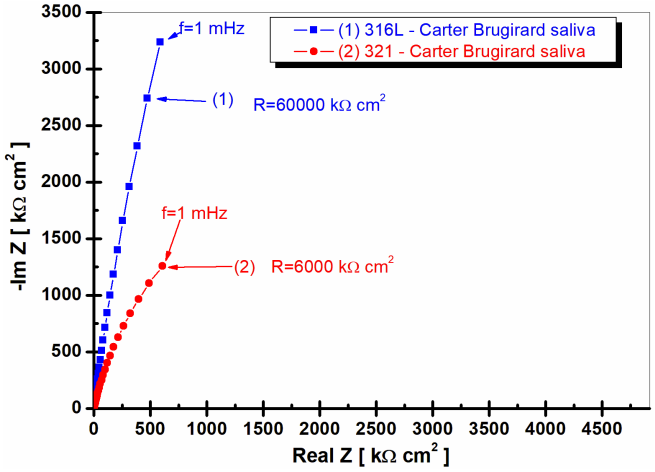

Fig. 5. Nyquist drawing of electrochemical impedance spectroscopy results recorded and fitted in Carter Brugirard saliva solution for: (1) 316 L stainless steel; (2) 321 stainless steel. Symbols are experimental results while the line represents the fitted curve

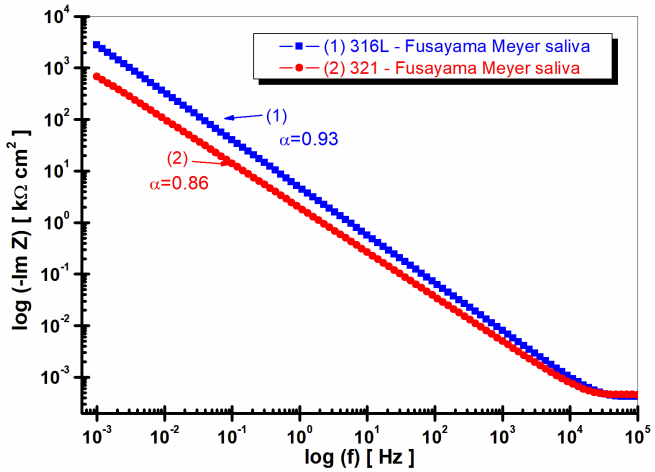

Fig. 6. Electrochemical impedance spectroscopy results in Fusayama Meyer saliva showing log (–ImZ) vs. log (f) in logarithmic scale to evaluate a impedance parameter for: (1) 316 L stainless steel; (2) 321 stainless steel

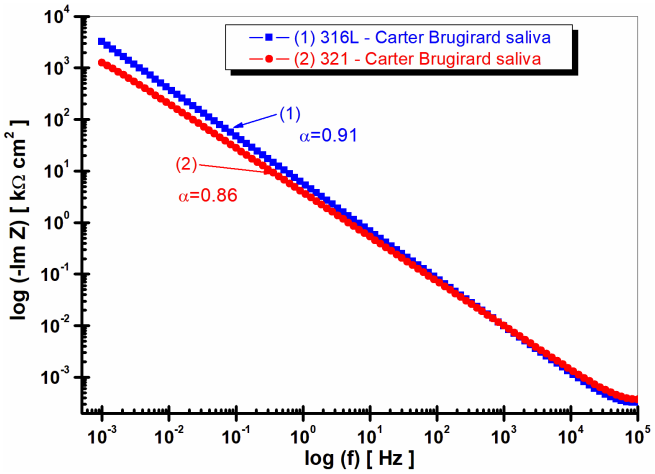

Fig. 7. Electrochemical impedance spectroscopy results in Carter Brugirard saliva showing log (–ImZ) vs. log (f) in logarithmic scale to evaluate a impedance parameter for: (1) 316 L stainless steel; (2) 321 stainless steel

As the imaginary part of the impedance is independent of the electrolyte resistance, the slope is constant throughout a large frequency range [22-24], Figs 6 and 7.

Thus, this type of electrochemical impedance data allows the evaluation of the value of the parameter α for the constant phase element impedance, CPE, (Z_{CPE}) which can be described by equation (1) [22-23] as follows:

$$Z(\omega) = R_e + \frac{1}{Q \cdot (j \cdot \omega)^{\alpha}} \quad (1)$$

where: Z is the impedance of the CPE element, j is the imaginary unit. The parameters α and Q are constant in relation to the frequency, $\omega = 2\pi f$ is the angular frequency.

When $\alpha = 1$, Q has the units of a capacitance, for example $\mu F/cm^2$, and represents the capacity of the interface. When $\alpha \neq 1$ the system shows the behavior attributed to inhomogeneous surfaces or time constants continuously distributed for charge transfer reactions [22-27].

Thus an α parameter value of 0.93 is obtained for 316L stainless steel in Fusayama Meyer saliva while for 321 stainless steel the value of the α parameter is slightly smaller, being 0.86 as it is shown in Fig. 6, curve (1) and curve (2).

By immersion in Carter Brugirard saliva solution, Figure 7, curve (1) and curve (2) the 316L stainless steel reveals an α parameter value of 0.92 while 321 stainless steel show a α parameter value of 0.86 being similar with those obtained in Fusayama Meyer saliva, Fig. 6, curve (2).

The parameter of the electrochemical impedance that represents an important criterion for the comparison of the stainless steels immersed in saliva solutions is the specific polarization resistance, R_p, which was obtained following the simulation (fitting) of the experimental results, using the equivalent circuit shown in Fig. 8, considering a solid electrode, stainless steel, in contact with the solution that simulates the fluid in the human body, respectively saliva. The electrical equivalent circuit is similar to the one proposed by the same authors to study the effect of fluoride toothpaste on 316L stainless steel immersed in Fusayama Meyer saliva [18].

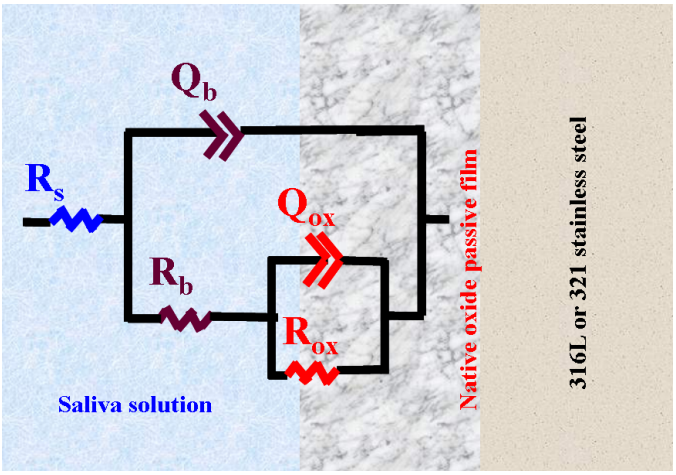

Fig. 8. Electrical equivalent circuit proposed to fit de electrochemical impedance Spectroscopy data of 316L and 321 stainless steels immersed in Fusayama Meyer and Carter Brugirard saliva solutions

The electrical equivalent circuit is composed by: R_s that is the resistance of the electrolyte (saliva), Q_{ox} is the constant phase element that describes the surface of the passive chromium oxide film in contact with saliva solution, R_{ox} that is the polarization resistance of the same oxide passive film, Q_b that is the constant phase element describing the interface of the bulk stainless steel, which is in contact with saliva through the passive film, R_b that is the polarization resistance of bulk stainless steel.

The electrochemical impedance spectroscopy measurements confirm quantitatively the better behavior of 316L stainless steel compared with 321 stainless steel in both types of tested saliva.

Thus the specific resistance, R = 59000 kΩ·cm^2, of 316L stainless steel immersed in Fusayama Meyer saliva is about 10 times higher than the specific resistance of 321 stainless steel immersed in the same saliva, R = 4400 kΩ·cm^2. These results are in accordance with the results obtained by monitoring the evolution of open circuit potential presented in the Figs. 2 and 3.

The specific resistance of 316L stainless steel in Carter Brugirard saliva solution, Fig. 5, curve (1) displays about the same value as those calculated in Fusayama Meyer saliva, R = 60000 kΩ·cm^2, while the specific resistance of 321 stainless steel in Carter Brugirard saliva solution, Fig. 5, curve (2) shows a value 10 times smaller than those of 316L stainless steel in the same saliva.

By measuring the electrochemical impedance, spectroscopy in the preclinical study of 316L and 321 stainless steel it can be conclude that the 316L stainless steel reveals a higher specific polarization resistance as compared with 321 stainless steel in both types of tested saliva solutions.

It is generally accepted that a higher value of polarization resistance means a smaller value of corrosion rate being inversely proportional.

4. Conclusions

A preclinical study is made to evaluate comparatively the corrosion resistance of two stainless steels, 316L and 321 in two types of saliva solutions, Fusayama Meyer and Carter Brugirard at different pH values.

From the monitoring of the open circuit potential, it resulted qualitatively information that the 321 stainless steel proved a lower corrosion behavior than the 316L steel registering more negative values of the free potential in both saliva solutions tested.

By measuring the electrochemical impedance spectroscopy in the preclinical study of 316L and 321 stainless steel it is revealed the better corrosion resistance of 316L stainless steel as compared with 321 stainless steel in both types of tested saliva solutions. The specific polarization resistance of 316L stainless steel resulted from fitting the electrochemical impedance experimental data revealed ten times higher values than those of 321 stainless steel in both types of saliva solutions.

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