THE EFFECT OF FLUORIDE CONTAINING TOOTHPASTE ON THE ELECTROCHEMICAL BEHAVIOR OF 316L STAINLESS STEEL FOR DENTISTRY APPLICATIONS IN THE HUMAN SALIVA

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ABSTRACT

The study aims to investigate the effect of fluorinated toothpaste added in Fusayama-Meyer saliva in order to evaluate the electrochemical behavior of 316L-SS for dentistry applications.

For electrochemical behavior in situ electrochemical measurements such as: Open circuit potential (OCP), Linear Polarization (PL), Potentiodynamic Polarization (PD) and Electrochemical Impedance Spectroscopy (EIS) were applied. The results show a comparative analysis of the electrochemical behavior and corrosion resistance of 316L-SS in human saliva containing high fluoride toothpaste for dentistry applications. From the electrochemical results it can be concluded that the addition of fluoride toothpaste in Fusayama-Meyer saliva decreases the corrosion resistance of 316L-SS and therefore will reduce the lifetime of dentistry structures or devices.

KEYWORDS: orthodontic devices; 316L stainless steel; corrosion; electrochemical methods; saliva; toothpaste

1. Introduction

Stainless steel AISI 300th series of steels has high rates of corrosion resistance, strength and flexibility. They can be used with equal success in the food [1], pharmaceutical industries [2] or dental medicine [3]. However, in recent years, interest in AISI 316L (316L-SS) has increased from economic considerations (low cost, reasonable strength, corrosion resistance and biocompatibility) [4-5]. For example, in dentistry, it is used in a variety of applications (endodontic files in root canal therapy, sterilized instruments, metal posts in root canal treated teeth, arch wires, temporary crowns and brackets in orthodontics) [5]. This can be attributed primarily to corrosion resistance. Moreover, this resistance concerns not only atmospheric phenomena, but also acidic and alkaline media present in the oral cavity of healthy or sick patients.

In the context of the mechanical systems, making orthodontic metallic devices and their subsequent use in the oral cavity for a long time, requires utmost attention to the corrosive process of the material in aggressive environments due to factors such as salivary pH, temperature, quantity of

microelements (F, Cl) and enzymatic activity of bacterial micro flora.

Consequences of the corrosive process represented by surface modification and increased roughness cause a decrease in the mechanical strength of the alloys in time [6-7].

Last but not least, the recommendations of the specialists regarding oral hygiene as a preventative treatment of orthodontic treatment should be considered, where dental brushing is the basis of the process of removing food debris and plaque accumulated around orthodontic appliances to counteract the development of dental and periodontal pathologies [8]. Among other things, the latest research demonstrates a better preventative result of diurnal and nocturnal brushing with Fluorine 5000 ppm fluoride toothpaste than the combination of once daily fluoride toothpaste 1000 ppm and rinse with sodium fluoride 500 ppm [9].

However, other studies appreciate the presence of sodium fluoride in products of oral hygiene, as initiator of the corrosive process by the formation of hydrofluoric acid (HF) after reacting of fluorine and hydrogen ions produced by bacteria, with role to destroy the protective oxide layer on the surface

orthodontic metal components [6, 10-11] or increase friction force [12]. In some recent studies, corrosion mechanisms of stainless steel have been examined in various solutions, including different artificial saliva [5, 13-16].

The purpose of this work is to evaluate the corrosion resistance of AISI 316L stainless steel in terms of their suitability for dentistry applications in two different artificial saliva with Fluoride as 1400 ppm toothpaste and non-fluoride one. Comparative corrosion evaluation was performed using electrochemical techniques as open circuit potential, potentiodynamic measurements and electrochemical impedance spectroscopy measurements at free potential. In the literature there is a lack of information regarding the influence of fluorinated toothpaste on the corrosion behavior of stainless steel

in saliva for dentistry applications. This research work aims to investigate the effect of fluorinated toothpaste added to human saliva on the corrosion behavior of 316L stainless steel used in orthodontic applications.

2. Materials and methods

2.1. Materials and methodology

In this experimental study, the samples of AISI 316L stainless steel purchased from Direct Line Inox, Bucharest in a form of sheets with the following dimensions 250 mm x 250 mm and 1.5 mm thickness, with compositions in mass fractions as shown in Table 1.

Table 1. Chemical composition in mass percent of the AISI 316L stainless steel

Chemical compositions (wt%)							
Chemical element	C	Mn	Si	Mo	Ni	Cr	Fe
316L SS	≤0.03	≤2	1	2.0-2.5	11-14	16.5-18.5	Bal.

Each group of the samples AISI 316L SS samples were investigated to one of two media: SFM (human Saliva Fusayama-Meyer) [4, 17] and SFM mixed with fluoride-containing toothpaste. The chemical composition of Fusayama Meyer saliva can be seen in Table 2.

Composition of fluorinated toothpaste (ParodontaxR) (1400 ppm F⁻ ion) describes these components: Sodium Bicarbonate, Aqua, Glycerin, Cocamidopropyl Betaine, Alcohol, Krameria Triandra (Ratanhia), Mentha Piperita Oil, Mentha Arvensis Oil, Echinacea Purpurea, Commiphora Myrrha, Chamomilla Recutita, Salvia Officinalis (Sauge) Oil,

Sodium Fluoride, Sodium Benzoate, Xanthan Gum, Sodium Saccharin, Limonene, CI 77491.

This study also involves a method of calculating the physiological proportions of human saliva and fluorinated toothpaste, used in another research field, where it proposes a mixture of paste and solution in a ratio of 1:4 (w/v) [6].

In this experiment it was used a solution of human saliva in volume of 150 mL mixed with 37.5 g fluorinated toothpaste. The reported volume between saliva and toothpaste represents the quantity of oral fluid exposed to a healthy person during a 3-4 minute dental brushing, where the average normal stimulated salivary secretion is 1 mL / minute [18].

Table 2. Chemical composition of Fusayama-Meyer saliva

Nr. crt.	Compound	Saliva Fusayama Meyer [g/L]
1	NaCl	0.4
2	KCl	0.4
3	$CaCl_2$	0.8
4	$NaH_2PO_4*12H_2O$	0.79
5	UREA	1
6	**pH**	**5.7**

The samples used as the working electrodes were cut into 25 x 25 mm plate with 1.5 mm thickness and solder with an electrical cable to have electrical contact and insulated with epoxy resin leaving a working area exposed for electrochemical

tests resulted at 225 mm² (15 mm x15 mm). The sides and the conductive cable contact area were protected by an inert resin layer. The electrochemical measurements were carried out with three-electrode electrochemical station in a 250 mL cell and managed

by hardware device VoltaLab PGZ 100 with software controlled VoltaMaster 4 by a personal computer. In the electrochemical cell, the AISI 316L stainless steel work electrode (WE) and the auxiliary electrode (AE) consisting of a Pt-Rh grid were spatially arranged parallel and on the same distances between electrodes. The reference electrode Ag/AgCl with KCl saturated solution (E = +199 mV) is placed halfway between WE and AE [19].

Before each experiment, the AISI 316L stainless steel samples were cleaned with ethanol 99.3% after then rinsed in distilled water and dried. For each experiment it was established a volume of 150 mL solution. All experiments have been conducted at room temperature of 25 °C.

The electrochemical methods were focused on the following corrosion tests: Open circuit potential (OCP) measured for a period of 720 minutes and monitored over time until it reached a stable state value relative to the Ag/AgCl reference electrode (RE).

The linear and potentiodynamic polarization were performed after 28 hours of immersion of the sample and consisted of imposing a potential amplitude of ±50 mV around free potential or imposing a variable potential (range from -1 V to +1.5 V/Ag/AgCl) between the working electrode (WE) and the reference electrode (RE) with a scan rate: 1 mV/s.

Measurements of Electrochemical Impedance Spectroscopy makes it possible, without disturbing the nature of the flow of operation, to study the kinetics and mechanism of corrosion processes, passivation mode and the formation of protective films on metals, as well as the adsorption behavior of inhibitors. Electrochemical Impedance Spectroscopy (EIS) after 12 hours of immersion were performed in a spectrum value from 100 kHz to 1 mHz, where the alternate applied signal has a sine wave amplitude of 10 mV with a frequency per decade of 10 Hz and 0.1 s delay before integration. All recorded EIS measurements were analyzed as Nyquist and Bode diagrams using the ZView 3.4e software for fitting the experimental data. To verify reproducibility, each experiment was repeated four times.

3. Results and discussions

3.1. Open circuit potential (OCP)

The variation of the open circuit potential is used as a criterion for determining the corrosion behavior tendency of a material in an oxidizing environment. OCP measurements of AISI 316L stainless steel immersed in saliva Fusayama Meyer and SFM with fluorinated toothpaste are presented in Figure 1.

The physico-chemical characteristics of prepared solutions used for corrosion investigations were measured with a multi-parameter analysis device CONSORT C-533 were used. The results are displayed in Table 3.
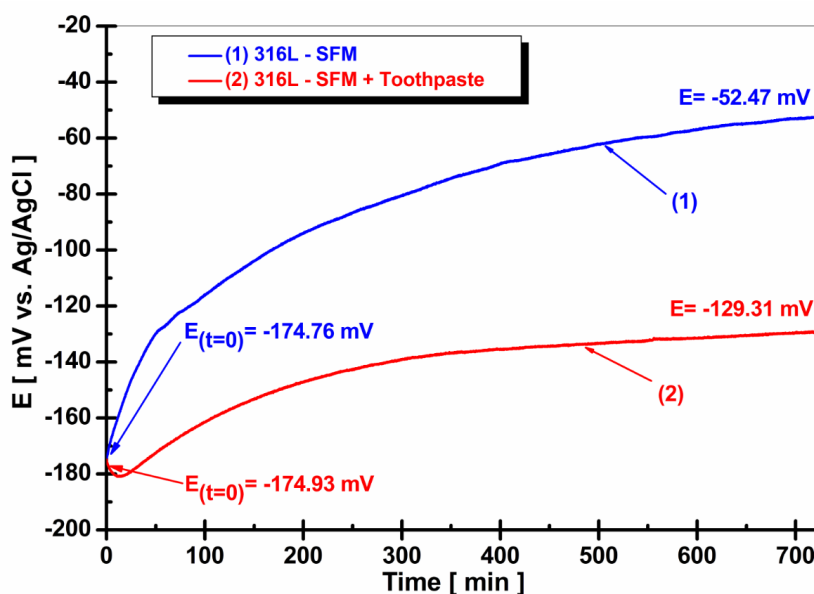

Fig. 1. *Evolution of open circuit potential during 12 hours of immersion of 316L stainless steel in: (1) Saliva Fusayama-Meyer; (2) Saliva Fusayama-Meyer with fluorinated toothpaste*

Table 3. *Characteristics of Fusayama Meyer saliva*

Simulated Body Fluid	pH	Salinity	Conductivity [mS/cm]
Saliva Fusayama Meyer	5.7	1.3	2.6
Fusayama Meyer + Fluorinated toothpaste	8.1	26.3	42

From Figure 1, the open circuit potential recorded for 12 hours in two different pH solutions (5.7 and 8.1) show that the starting values or the immersion time values of open circuit potential are very close, respectively -174.76 mV vs. Ag/AgCl in SFM with pH 5.7 and -174.93 mV vs. Ag/AgCl in SFM with toothpaste (pH 8.1). The transition tendency to passive potentials in SFM with pH 5.7 is at more positive values reaching a steady state value of -52.47 mV vs. Ag/AgCl. Comparing to the open circuit potential in fluorinated medium with pH 8.1, the passive potential is established to more negative values and the steady state value is reached at -129.31 mV vs. Ag/AgCl at the end of measurement.

In order to determine the influence of the pH factor besides F⁻ ion, the samples were tested with other electrochemical methods.

3.2. Linear polarization (LP)

From the linear polarization diagram, quantitative information on the polarization resistance and corrosion currents can be extracted from the curve slope according to the Stern- Geary equation [5].

$$i_{cor} = \frac{B}{R_p} \qquad (1)$$

While the Stern-Geary parameter B was calculated using equation:

$$B = \frac{b_a |b_c|}{2.303(b_a + |b_c|)} \qquad (2)$$

where: i_{cor}= corrosion current density; R_p=polarization resistance; b_a and b_c are the Tafel slopes for anodic and cathodic reactions on linear polarization curves. The increase of polarization resistance means the decrease of corrosion current, therefore the decrease of corrosion rate.

In Figure 2, the linear polarization curves of AISI 316L SS are shown. It is observed that the corrosion potential (Ecor) for stainless steel immersed in Fusayama Meyer saliva mixed with fluorinated toothpaste with pH 8.1 is shifted to more negative value, mV vs. Ag/AgCl as compared with corrosion potential revealed by stainless steel in Fusayama Meyer without toothpaste with pH 5.7, mV vs. Ag/AgCl.
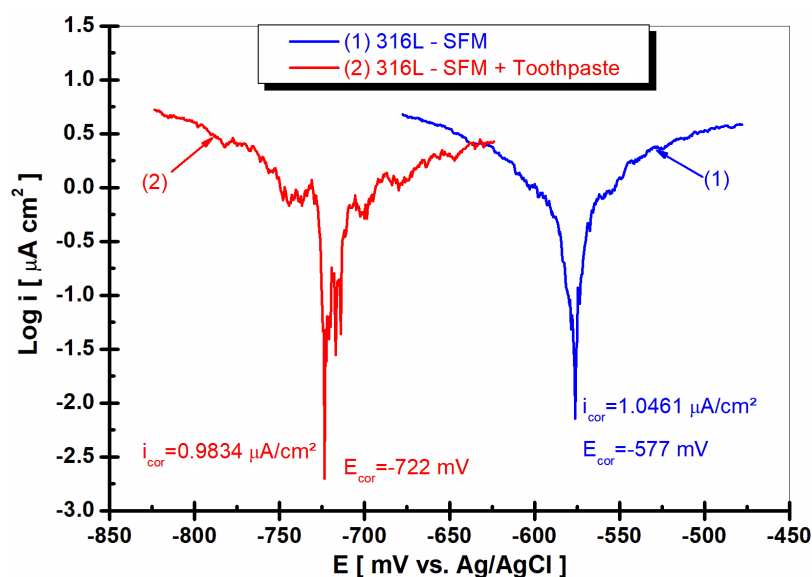

Fig. 2. *Linear polarization diagrams around free potential of 316L stainless steel in: (1) Saliva Fusayama-Meyer; (2) Saliva Fusayama-Meyer with fluorinated toothpaste at a sweep rate of 1 mV/s*

The corrosion current density reveals about the same values for stainless steel, both values being in the same order of magnitude as it can be seen in Fig. 2.

3.3. Potentiodynamic polarization

Potentiodynamic polarization diagrams were performed in Fusayama Meyer solution with and without fluorinated toothpaste. The results are presented in Figure 3 (a, b). Figure 3a show the entire domain of current density and potential while Figure 3b show a zoom in the range of lower current densities in order to observe better the passive domains of stainless steel immersed in saliva SFM and saliva SFM mixed with toothpaste.
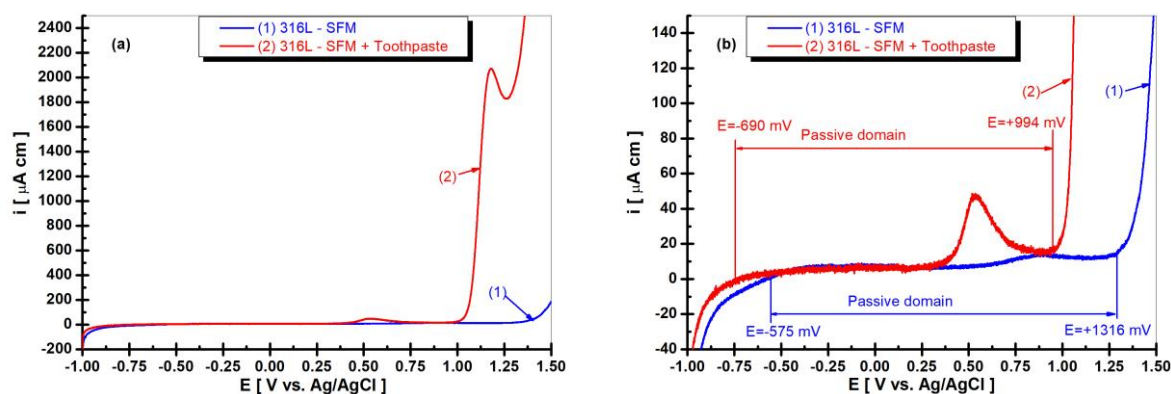

Fig. 3. *Potentiodynamic polarization diagrams of 316L stainless steel performed at a sweep rate of 1 mV/s in: (1) Saliva Fusayama-Meyer; (2) Saliva Fusayama-Meyer with fluorinated toothpaste*

As it is shown in Figure 3a the current density in transpassive domain of stainless steel immersed in saliva mixed with fluorinated toothpaste increases rapidly having higher values as compared with the current density of stainless steel in transpassive domain corresponding to Fusayama Meyer saliva without toothpaste. The passive domain of stainless steel immersed in Fusayama Meyer solution is wider extending over 1316 mV as it can be seen in Figure 3b. When human saliva is mixed with fluorinated toothpaste the passive domain of 316L stainless steel becomes narrower stretching only on 994 mV. It appears also that localized corrosion through passive film occurs when saliva is mixed with fluorinated toothpaste, Figure 3b, diagram (2).

3.4. Electrochemical impedance spectroscopy

In this section, the results obtained by the impedance spectroscopy method complement the open circuit and polarization measurements. To more clearly identify the features of the electrochemical corrosion behavior of AISI 316L stainless steel in human saliva environment with and without addition of fluorinated toothpaste, tests were performed to measure the impedance of an electrochemical cell when a small amplitude sinusoidal voltage is applied to it. As a result of the EIS measurements and its

graphical dependence of $Z = f(\omega)$, where ω is the angular frequency, in the coordinates of complex ohmic plane, the real component (Re Z) is plotted along the x axis, and the imaginary component of the resistance (- Im Z) is plotted along the y axis [20]. Figure 4 shows the impedance spectrum in the Nyquist graphs, with a higher specific resistance of 316L stainless steel in Fusayama-Meyer saliva, R= 4370 as compared with the specific resistance obtained in human saliva mixed with fluoride toothpaste, R = 1200 kohm·cm^2.

To simulate and fit the EIS experimental results an equivalent electrical circuit model is proposed to express the interface of stainless steel in contact with human saliva. Characterizing the corrosion processes occurring on their surface. The impedance is expressed by the following equation [21-22]:

$$Z_{CPE} = \frac{1}{Q(j\omega)^{\alpha}} \qquad (3)$$

where: Q is the frequency-independent real constant of the CPE in F cm-2 sα-1, ω is the angular frequency ($\omega = 2\pi f$) in rad s^{1-}, f is frequency Hz, j is the imaginary number, $j = \sqrt{-1}$, α is related to the angle of rotation of a purely capacitive line on the complex plane plots.
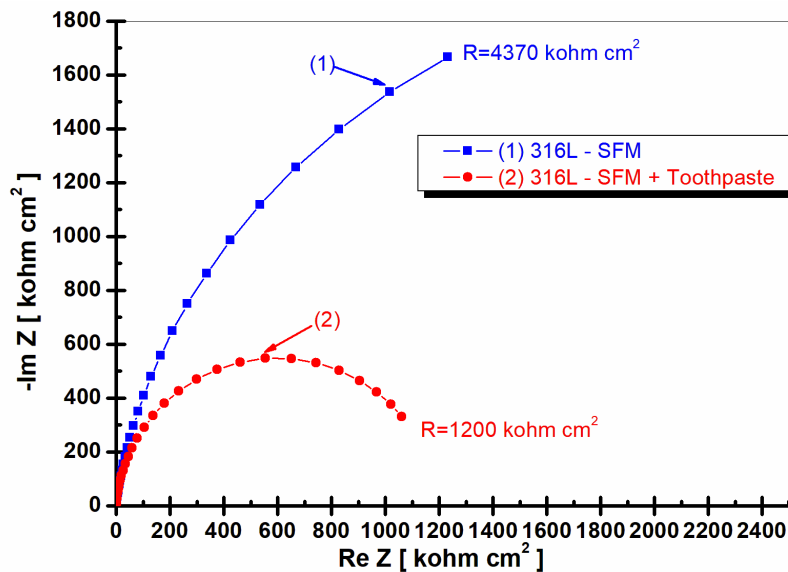
Fig. 4. *Nyquist graphs of the impedance results for the AISI 316L stainless steel immersed in: (1) Saliva Fusayama-Meyer; (2) Saliva Fusayama-Meyer with fluorinated toothpaste*

The time constant dispersion, CPE is attributed to capacity dispersion or to capacity change with frequency. For this research work the constant phase elements (CPE) could express the irregularity of the electrode surface. The value of α is associated to the non-uniform distribution of current as the result of surface inhomogeneity (roughness, structure, defects). The parameter α can takes values from -1 to 1 [23]. In the case when $\alpha \neq 1$, the system reveals a behavior that attributes heterogeneity or the continuously distributed time constants for charge-transfer reactions [5].

The modified Randles circuit with two-time constants, with schematic presentation in Fig. 5, was proposed to fit the EIS experimental results. In this circuit R_s is the solution resistance, CPE_1 is an element of the first constant phase, R_1 is the specific resistance for the first time constant, R_2 is the solution and the corrosion product film resistance and CPE_2 establish the second element constant phase [24]. The first time constant (R_1-CPE_1) is connected with bulk steel passive film interface controlling the dissolution of steel elements and also formation of passive film on stainless steel surface. The second time constant (R_2, CPE_2) describes the passive film/saliva solution interface. This interface controls and at the same time slows down the corrosion degradation process.
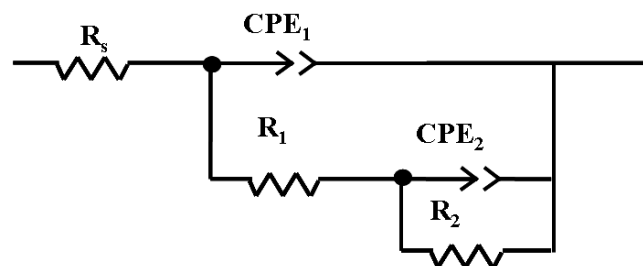

Fig. 5. *The equivalent electrical circuits of AISI 316L stainless steel surface used for better fitting and simulation of electrochemical experimental measurements of the impedance spectra*

The proposed equivalent electrical circuit fits well the Nyquist impedance experimental data but also the Bode plots and admittance plots as module Z versus frequency and phase element versus frequency. The Bode plots, Figure 6 (a) and (b) are displayed an acceptable agreement between experimental and simulated data, thereby validating the selected equivalent circuit model.
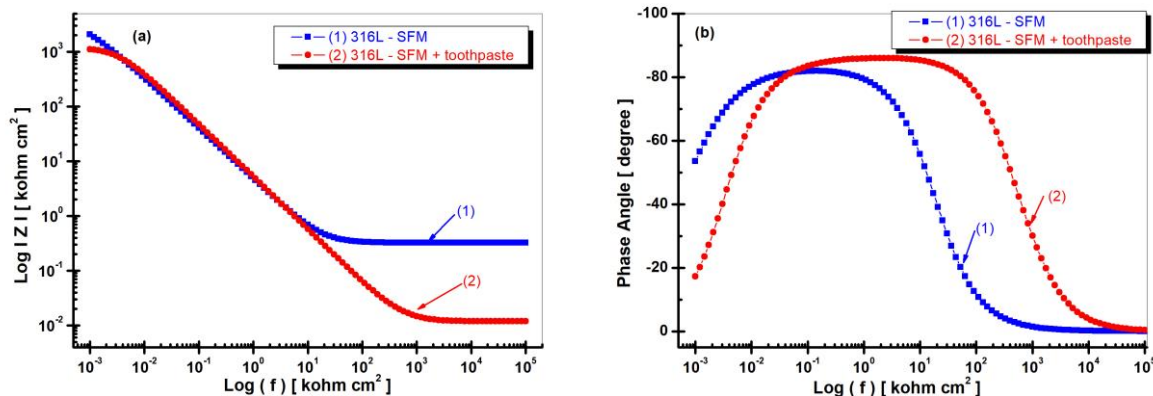
Fig. 6. *Electrochemical Impedance Spectroscopy results (symbols) and fitting diagrams (plain lines) in the Bode coordinates for the AISI 316L stainless steel immersed in: (1) Fusayama Meyers saliva; (2) Fusayama-Meyer saliva mixed with fluorinated toothpaste. (a) - module Z vs. logarithm of frequency and (b) phase angle versus logarithm of frequency*

Table 4 summarizes the values of the circuit parameters obtained from the best fit with the experimental impedance diagrams.

The results obtained after fitting the EIS data using the proposed equivalent circuit (EC), are describing major or minor differences between the two tested solutions. The R values showed on Nyquist impedance data from Figure 4 are values obtained by summing R1 and R2 for respective saliva solution. The R values for SFM solution and for SFM mixed with fluorinated toothpaste are of the same order of magnitude but with slower decrease for 316L stainless steel immersed in Fusayama Meyer saliva mixed with fluorinated toothpaste (about four time smaller) indicating a slower increasing of corrosion rate due to fluor ions containing the toothpaste.

Table 4. *Fitted values for the different elements of the electrical equivalent circuits for the impedance experimental results of 316L stainless steel immersed in Fusayama Meyer saliva with and without fluorinated toothpaste*

Elements of the equivalent circuit	R_1 [$k\Omega$ cm^2]	CPE_1 [F cm^{-2}]	R_2 [$k\Omega$ cm^2]	CPE_2 [F cm^{-2}]	α	R [$k\Omega$ cm^2]
Fusayama-Meyer saliva	129	4.38E-7	4241	3.77E-5	0.92	4370
Fusayama-Meyer saliva + fluorinated toothpaste	72	2.08E-5	1128	1.20E-5	0.88	1200

Tables 4 indicates values of the α element of 0.92 with the tendency towards pure capacitive behavior for stainless steel immersed in Fusayama Meyer saliva. A slower value of *α* parameter of 0.88 is obtained after fitting the impedance results of 316L stainless steel immersed in Fusayama Meyer saliva mixed with fluorinated toothpaste.

4. Conclusion

The study presents the corrosion behavior of AISI 316L stainless steel in Fusayama Meyer saliva and the effect of fluorinated toothpaste on corrosion resistance. The results of open circuit potential evolution reveal that AISI 316L stainless steel immersed in Fusayama Meyer saliva show a passive state with the tendency to slow increase to more positive values as compared with the evolution of open circuit potential of stainless steel immersed in saliva mixed with toothpaste, which is shifted from the beginning of immersion to more negative values and the steady state value is stated at more negative value also.

Analyzing the linear polarization diagrams it is concluded that the corrosion potential is obtained at more negative value for AISI 316L Stainless Steel immersed in Fusayama Meyer saliva as compared with saliva mixed with fluorinated toothpaste, even if the corrosion current densities reveal the values of same order of magnitude.

The polarization curves in the potentiodynamic regime denoted that the passive domain in the solution without the toothpaste is larger than those revealed in saliva mixed with fluorinated toothpaste.

From the Electrochemical Impedance Spectroscopy can be concluding that AISI 316L SS immersed in artificial Fusayama Meyer saliva have a higher value of specific polarization resistance as compared to human saliva mixed with toothpaste.

Therefore, the recommendations of dentists regarding dental brushing with fluorinated toothpaste for orthodontic patients require a readjustment of the oral hygiene products suggested with those without the fluorinated component.

Acknowledgments

Disclosure of interest

The authors declare that they have no competing interest.

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