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Short Communication

316L Stainless Steel Alloys for Orthodontic Application: Effect of Fluorinated Toothpaste on the Corrosion Behavior in Human Saliva

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Orthodontic implanted wires are made of different stainless steels, to regulate the teeth. The fluorinated toothpastes used during the period of the treatment may induce a corrosive effect on these stainless steels. Hence, the main objective of this research work is to investigate and evaluate the effect of fluorinated toothpaste on the corrosion behavior of 316L stainless steel in Carter-Brugirard human saliva. Electrochemical methods such: Open circuit potential, potentiodynamic polarization and electrochemical impedance spectroscopy; have been used to evaluate the corrosion behavior of stainless steel in saliva and saliva mixed with fluorinated toothpaste. The OCP value recorded for 316L SS immersed in saliva mixed with fluorinated toothpaste was lower than 316L SS in saliva without fluorinated toothpaste. This behavior confirms a high reactivity of 316L SS in presence of fluorinated toothpaste. Electrochemical impedance spectroscopy (EIS) results indicate a decreasing trend in specific polarization resistance of stainless steel 316L in presence of fluorinated toothpaste. The results show that the addition of a small quantity of fluorinated toothpaste in Carter-Brugirard human saliva affects the corrosion resistance of 316L stainless steel.

Keywords: Orthodontic applications, toothpaste, stainless steel, corrosion, human saliva, electrochemical impedance spectroscopy.

1. INTRODUCTION

Biocompatible materials should not cause the development of infectious diseases, cause the development of a local inflammatory reaction and affect the functioning of tissues, while ensuring the preservation of their functional characteristics throughout life [1]. Biological compatibility is a term widely used in the science of modern medical materials. At the Second Conciliation Conference in

Liverpool (UK), biocompatibility was defined as: "*the ability of a material to perform with an appropriate host response in a specific application*" [2]. Criteria are established that determine the biocompatibility of materials: the absence of toxic, immunogenic, genotoxic and carcinogenic effects.

In modern medicine, biotechnological products and systems are widely used and studied, in which various elements and parts interact with biological fluids, soft and hard tissues of the body. It mainly applies to products for cardiovascular surgery, orthopedics, dental and reconstructive surgery, ophthalmology. The materials of these products must have a certain complex of biological, physical-chemical, medical and technical properties, giving them a certain level of compatibility with the biological environment.

Research in the field of biomedical materials and technologies is carried out in several main areas: study of the processes of interaction of materials with biological fluids and tissues, development of methods for the production of materials with surfaces in specific biocompatibility parameters, creation of quantitative methods for assessing the properties of biocompatible materials and products, improving the methods of experimental and clinical use of products made of biocompatible materials.

But the greatest importance in improving the efficiency of diagnostic processes, therapeutic treatment, and surgery, restoration of functions or replacement of organs and rehabilitation of the patient is the development of methods for producing materials and coatings with qualities of biological and mechanical compatibility.

It is known that the first orthopedic implants were made of iron-based alloys [3]. The mechanical and physical-chemical parameters of these materials are quite high, but they have a low level of biocompatibility and corrosion resistance in aggressive biological environments, which can lead to the development of various allergic and inflammatory reactions, which has limited their active use [4-6].

The first metal materials that were used successfully in orthopedics in the twentieth century were stainless steel and cobalt and chromium alloys. Stainless steels are resistant to a wide variety of corrosive environments due to their high chromium content, up to 12%. The presence of chromium determines the formation of a high-strength, self-healing and corrosion-resistant oxide film. Stainless steels are widely used in temporary trauma devices (staples, plates, screws) due to their relatively low cost, availability and easy handling. Due to their low wear resistance, stainless steel materials are not used in the manufacture of joint prostheses. Joint prostheses are made of Co-Cr-Mo alloys (ASTM F75) [7]. These alloys have good mechanical properties, high corrosion resistance and wear, but the disadvantage is the lack of surface biological stimulation [7].

At this time, the use of any medical device based on metals and alloys, especially for orthodontics and dentofacial orthopedics, is impossible without the preclinical assessment of its chemical, biological and mechanical properties. Today, wires, brackets or other orthodontic metal devices that allow the recovery of bone fragments from jaw fractures have no rival in terms of mechanical strength and biocompatibility. The advantage of using metals and alloys in orthopedics is high reliability, long service life and high functionality. The anticorrosive properties of the material are the main advantage, which determines the biocompatibility of metallic biomaterials and their functionality [8].

For example, 316L stainless steel, especially as orthopedic and orthodontic devices, has a high level of mechanical strength and corrosion in physiological environments. Currently, the properties of the 316L-SS material, in terms of surface resistance in the presence of human saliva and fluoridecontaining toothpastes are not sufficiently studied.

In the literature we found some studies which treat the corrosion of titanium brackets in fluoride solutions [9], fluoride contain tea and toothpaste [10], fluoride mouthwash [11].

The research work aims to investigate and to evaluate the effect of fluorinated toothpaste mixed with human saliva on the corrosion behavior of 316L stainless steel by electrochemical methods.

2. EXPERIMENTAL METHODS

For corrosion investigations it was used stainless steel 316L with a with chemical composition (wt): C, < 0.03 %, Cr, 16.5-18.5 %, Ni, 11-14 %, Mo, 2-2.5 %, Si, 1.0 %, Mn, 2.0 %, Fe, balance. Termination "L,, at stainless steel, means that the steel have a low content of carbon element. The stainless steel medical grade SS316L was purchased in the form of plates with the size of 25mm x 25 mm x 15 mm, establishing an active sample surface area of 4.25 cm^2. This was done by delimiting the surface with an epoxy resin. To have electrical contact on the samples, a copper electrical cable was used whose diameter was Ø 2.5 mm.

The experiments were done using a Potentiostat–Galvanostat PGZ 100 and the data were recorded with software VoltaMaster4. The electrochemical measurements such as Open Circuit Potential (OCP), Potentiodynamic polarization (PD), and Electrochemical Impedance Spectroscopy (EIS) were carried out to access the anticorrosive characteristics of the stainless steel medical grade SS316L.

The OCP measurements were monitored with the exposure time of 12 hours, meas period 0.2 s until has been obtained a stable potential vs. Ag/AgCl reference electrode.

Potentiodynamic polarization diagrams (PD) are performed in the potential range from -1000 mV to +1500 mV versus Ag / AgCl at a potential scanning rate of 1 mV / s.

EIS spectra were recorded in the frequency range from 100 kHz to 1 mHz, with a sinusoidal signal amplitude of 10 mV, frequency per decade: 10 Hz and delay before integration 0.1 s.

The EIS spectra were fitted using ZView 3.4f software and the quality of the fitted results was evaluated with the chi-square value, which was in order of 10^{-3}. Each experiment was repeated at least four times to verify the reproducibility of the experimental data.

A three-electrode cell specially made of glass it was used for corrosion investigations consisting of: auxiliary electrode made by Pt, reference electrode Ag/AgCl with KCl saturated solution and working electrode (SS316L). Before corrosion investigations the samples was cleaned with alcohol and distilled water.

The used fluorinated toothpaste (1400 ppm F^- ion) has the following composition: 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. The method of calculating the physiological proportions of saliva and fluorinated toothpaste, used in the literature is a mixture of paste and solution in a ratio of 1:4 (w/v) [12]. The reported volume represents the quantity of oral fluid exposed to a healthy person during 3-4 minutes of dental brushing, where the average normal stimulated salivary secretion is 1 mL / minute [13]. During the research work it was used a solution of Carter-Brugirard saliva (with chemical composition shown in Table 1) in volume of 150 mL and Carter-Brugirard saliva mixed with 37.5 g fluorinated toothpaste. All reagents used in the preparation of the solutions were of analytical purity, purchased from Lach:ner company.

Table 1. Chemical composition of Carter-Brugirard saliva.

Nr. Crt.	Compound	Saliva Carter Brugirard g / L
1	NaCl	0.7
2	KCl	1.2
3	NaHCO3	1.5
5	$Na_2HPO_4*7H_2O$	0.26
7	KSCN	0.33
8	UREA	1.3
9	pH	8.1

To measure the physical-chemical characteristics of solutions before starting the electrochemical measurements it was used a multi-parameter analysis device CONSORT C-533 and results are display in Table 2.

Table 2. Physical - chemical properties of Carter-Brugirard saliva and saliva mixed with fluorinated toothpaste.

Simulated Body Fluid	pH	Salinity	Conductivity [mS / cm]
Carter Brugirard saliva	8.1	2.8	5.3
Carter Brugirard saliva + fluorinated toothpaste	8.3	32.5	50.8

3. RESULTS AND DISCUSSION

3.1. Open circuit potential (OCP)

The time variation of the open circuit potential is used as the first criterion for determining the corrosion behavior of a material in a corrosive environment.

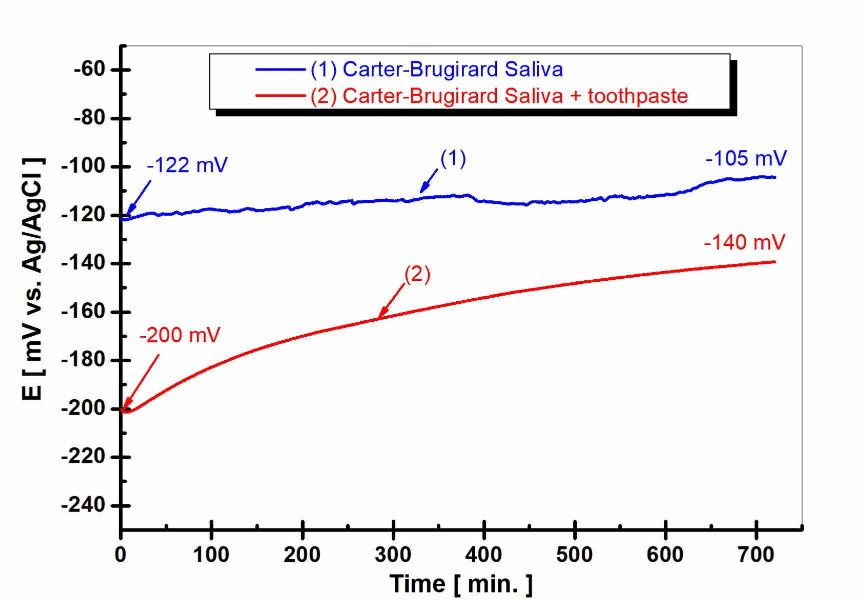

Figure 1. Open circuit potential evolution of 316L stainless steel during 12 h of immersion in: (1) Carter Brugirard saliva; (2) Carter Brugirard saliva mixed with fluorinated toothpaste

Figure 1 show the open circuit potential monitoring of 316L stainless steel immersed in Carter-Brugirard saliva and saliva mixed with fluorinated toothpaste. The results recorded during 12 hours of immersion in the two solutions with a slow different pH (8.1 and 8.3), reveal that at the time of immersion the values are different respectively: -122 mV vs. Ag / AgCl in Carter Brugirard saliva and -200 mV vs. Ag / AgCl in saliva mixed with toothpaste. The transition to the passivation state is made in both solutions. After 12 hours of immersion the free potential of 316L stainless steel shifts slightly to more positive values attaining a steady stable value at -105 mV vs. Ag / AgCl. The potential difference between the immersion time and the 12 hours, in the case of Brugirard Carter saliva is only 27 mV, $\Delta E = 27$. This could be explained by a good stability of 316L stainless steel in this type of saliva. The open circuit potential of 316L stainless steel immersed in saliva mixed with fluorinated toothpaste shifted also to more positive values during the 12 hours of measurements, but with a higher tendency, attaining the steady state value at -140 mV vs. Ag / AgCl. For 316L stainless steel the potential gradient during the 12 hours of immersion is higher, having the value of 60 mV, $\Delta E = 60$.

The same tendency of the open circuit potential to shift to more negative values in the presence of fluoride added to SBF tested solution was noticed in the scientific work of Reclaru et al.[14], but they worked with more acidic pH.

3.2. Potentiodynamic polarization (PD)

From the diagrams presented in Figure 2 it is observed that the value of the average passivation current density (i_{passiv}) on the passive domain of 316L stainless steel immersed in Carter Brugirard saliva is much lower, $i_{pasiv} = 5.7 \mu A / cm^2$, than the value of the average passivation current density for stainless steel immersed in mixed saliva with fluorinated toothpaste, $i_{pasiv} = 57.6 \mu A / cm^2$. The higher passivation current density of stainless steel in the presence of fluorinated toothpaste confirms that the native passive film from the stainless steel surface is very much affected being probably destroyed by toothpaste; therefore their restorations need a higher current density to re - passivation an active surface.

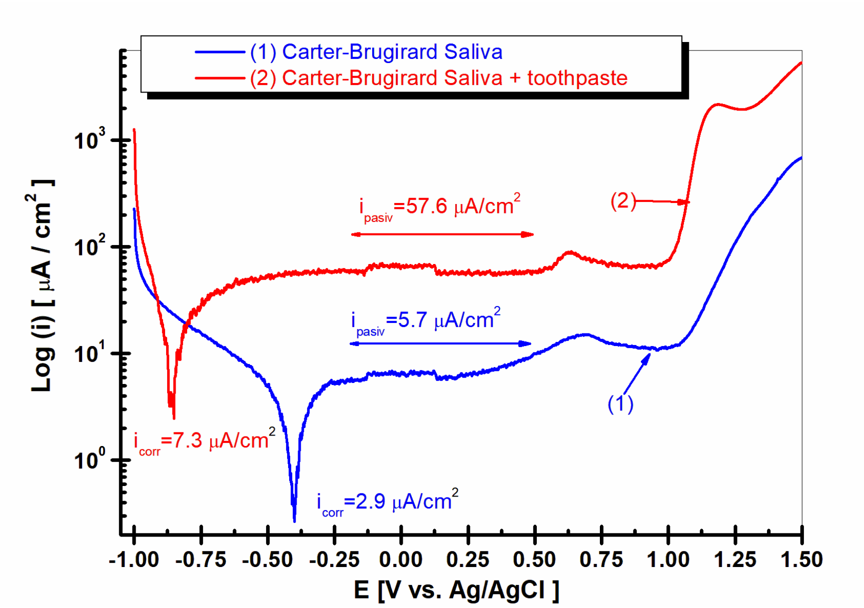

Figure 2. Potentiodynamic polarization diagrams of 316L stainless steel performed at a scan rate of 1 mV/s, immersed in: (1) Carter Brugirard saliva; (2) Carter Brugirard saliva mixed with fluorinated toothpaste

On the passive domain of stainless steel immersed in saliva mixed with fluorinated toothpaste shows few increases in the anodic dissolution current which could prove the installation of a preferential localized corrosion induced by the F^- ion in addition to the chloride ion already existed in the saliva solution. The anodic dissolution current of 316L stainless steel show also a higher value in saliva mixed with fluorinated toothpaste as compared with Carter Brugirard saliva without toothpaste.

A similar observation was reported in the study of Močnik et al.[15], by testing Ni-Ti alloy and AISI 304 in artificial saliva. The low presence of fluoride in saliva increases the passive current density. By increasing the fluoride concentration of 0.076 M [15], like the one found in toothpaste the passive region of both alloys become narrowing. As it is explained by M. Mirjalili et al [16], the increase of passivity current density can be attributed to the increase in oxide layer defects in the presence of fluoride ions and its oxid chemical dissolution [16].

For determination of corrosion current, Tafel extrapolation method was used [17]. The resulted corrosion current densities are different and could give us information about the negative effect of fluorinated toothpaste on the corrosion resistance of 316L stainless steel. The corrosion rate expressed in $\mu A/cm^2$ is about two times higher for 316L stainless steel immersed in Carter-Brugirard saliva mixed with fluorinated toothpaste, Figure 2.

3.3. Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) is a non-destructive technique and was performed to characterize the corrosion behavior of 316L stainless steel immersed in Carter-Brugirard saliva and Carter Brugirard saliva mixed with fluorinated toothpaste.

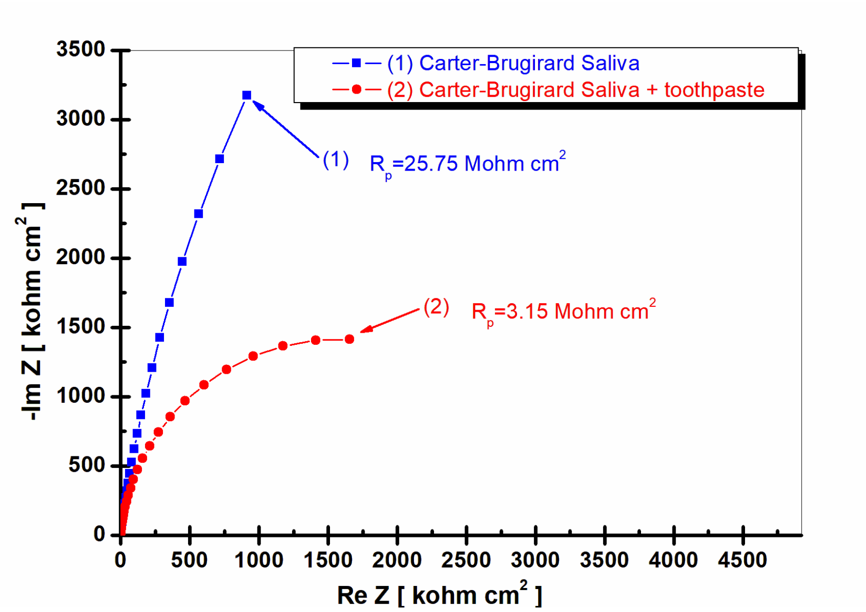

Figure 3. Nyquist plots of electrochemical impedance spectroscopy results of 316L stainless steel immersed in: (1) Carter Brugirard saliva; (2) Carter Brugirard saliva mixed with fluorinated toothpaste

Data recorded for 316L stainless steel immersed in both solutions were displayed as a Nyquist diagram as shown in Figure 3.

After fitting the specific polarization resistance, showed on Figure 3, could be evaluated with the best fitted equivalent electrical circuit drowns in Figure 4. The specific polarization resistance of 316L stainless steel immersed in Carter-Brugirard saliva mixed with fluorinated toothpaste is about one order of magnitude lower than that of stainless steel immersed in Carter-Brugirard saliva without toothpaste.

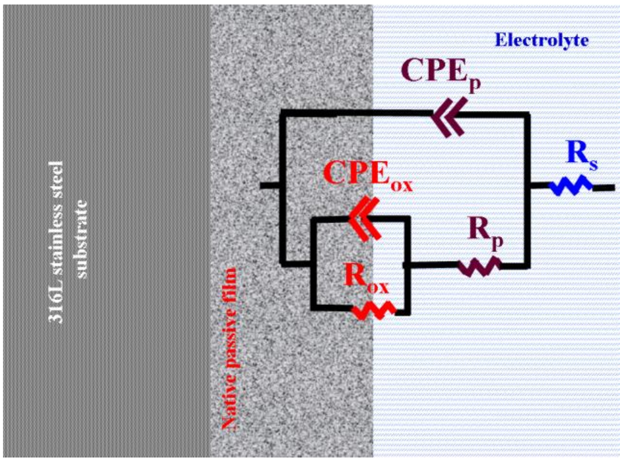

Figure 4. Equivalent electrical circuit resulted for fitting the impedance results of 316L stainless steel in corrosive environment of Carter-Brugirard saliva and Carter-Brugirard saliva mixed with fluorinated toothpaste

The proposed equivalent electrical circuit from Figure 4 takes into account the corrosion reactions going on the 316L stainless steel surface. The electrical equivalent circuit is similar with the optimal model proposed by Fekry et al. [18], when tested the 316L stainless steel rod by electrochemical impedance spectroscopy method in aqueous humor solution prepared with and without some drugs addition [18].

The surface is natively covered with a very thin layer of oxide predominately formed by chromium oxide, which slows down the corrosion process. Therefore in direct contact with the corrosive environment is the passive oxide film interface expressed in Figure 4 by the specific oxide resistance, R_{ox} in parallel with the constant phase element CPE_{ox}, which replaces the double layer capacitance for inhomogeneous surfaces. The corrosion anodic reaction of bulk stainless steel occurs through passive film and the final total specific resistance of degradation process is expressed by R_p in parallel with CPE_p, from Figure 4. The constant phase element (CPE) replaces the double layer capacitance in the impedance equation, following the equation [19-20]

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

Where: Q is the frequency-independent real constant of the CPE, j is the imaginary number, ω is the angular frequency ($\omega = 2\pi f$, f being the frequency in Hz).

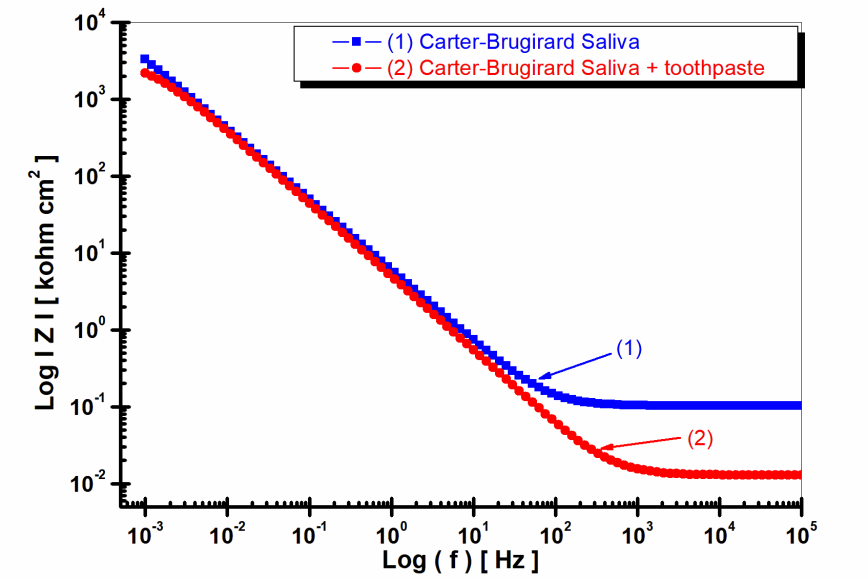

Figure 5. Impedance modulus of resulted and fitted impedance data for 316L stainless steel immersed in: (1) Carter Brugirard saliva; (2) Carter Brugirard saliva mixed with fluorinated toothpaste. Symbol represents impedance results and line is the fitted diagram

In Figure 5 and 6 are depicted the Bode representation of electrochemical impedance spectroscopy.

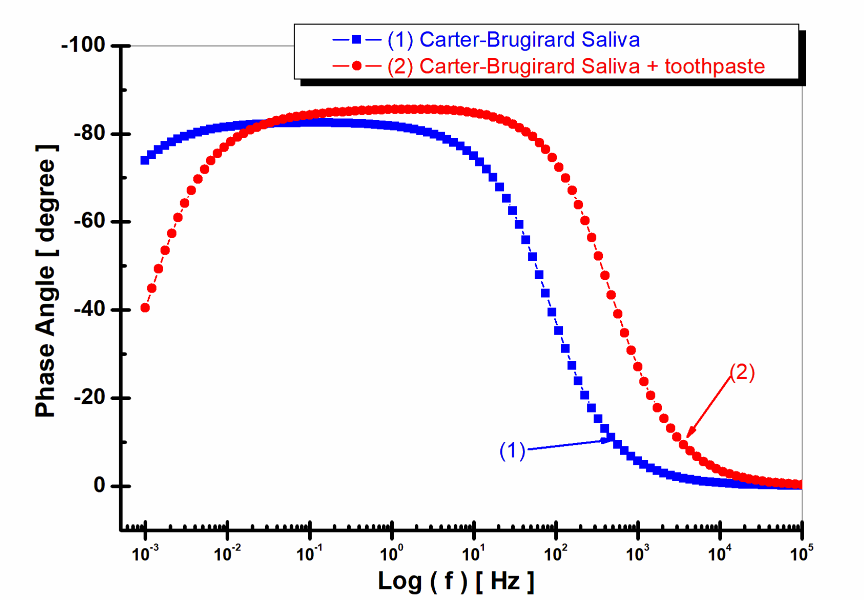

Figure 6. Phase angle of resulted and fitted impedance data for 316L stainless steel immersed in: (1) Carter Brugirard saliva; (2) Carter Brugirard saliva mixed with fluorinated toothpaste. Symbol represents impedance results and line is the fitted diagram

Table 3 shown the values obtained for the different elements of the electric equivalent circuits used to fit the electrochemical impedance spectra for SS316L surface immersed in saliva and saliva mixed with fluorinated toothpaste solutions.

Table 3. Values for the different elements of the electric equivalent circuits whose response fitted the data obtained for the 316L stainless steel surface, evaluated from EIS in saliva solutions.

Elements of the electric equivalent circuits	Carter Brugirard saliva	Carter Brugirard saliva + fluorinated toothpaste
R_s (Ω cm^2)	111.5	11.25
CPE_p (F cm^2)	2.90 x 10^{-5}	1.86 x 10^{-5}
α_p	0.95	0.93
R_p (MΩ cm^2)	24.35	2.02
CPE_{ox} (F cm^2)	4.29 x 10^{-5}	1.11 x 10^{-5}
α_{ox}	0.99	0.91
R_{ox}	1.40	1.13

The Bode representation of EIS measurements provides a clearer description of the behavior of the electrochemical system dependent of frequency in comparison with Nyquist representation. At low and medium frequency a high impedance value for SS316L immersed in Carter Brugirard saliva show a higher ohmic resistance in this electrolyte, as compared to the fluoride electrolyte. It can be noted that both curves are relatively close being in the same order of magnitude. Also from Figure 6 can be seen that the phase angle of both curve are also close in value illustrated a degree of phase angle close to -80 revealed a near capacitive response with a slow decrease of phase angle in the presence of toothpaste. This behavior of decreasing the phase angle was also observed by Fekry et al. [18] for 316 SS in aqueous humor solution [18] by increasing the concentration of drugs in solution.

4. CONCLUSIONS

The study presents the corrosion behavior of AISI 316L stainless steel in Carter-Brugirard saliva with or without fluorinated toothpaste intended for dental application. The evolution open circuit potential results reveal that 316L stainless steel immersed in Carter Brugirard saliva show a more positive value as compared with the open circuit potential of the steel immersed in saliva mixed with Fluoride toothpaste.

Analyzing the polarization curves in the potentiodynamic regime it results that the passivation current density is much higher on entire passive domain for saliva mixed with fluorinated toothpaste revealing that this kind of fluorinated toothpaste affects the passive film of stainless steel.

From the Electrochemical Impedance Spectroscopy can be conclude that 316L stainless steel immersed in Carter Brugirard saliva have a higher value of specific polarization as compared with the specific polarization resistance revealed in saliva mixed with fluorinated toothpaste.

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

CREDIT AUTHORSHIP CONTRIBUTION STATEMENT

Lidia Benea: Conceptualization, Methodology, Writing- Reviewing and Editing. Veaceslav Neaga : Investigation, Writing- Original draft preparation, Software, Validation. Andrada Alexandru: Visualization, Investigation, Software.

DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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