Electrochemical Study of Three Stainless Steel Alloys and Titanium Metal in Cola Soft Drinks

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ABSTRACT

Stainless steels and titanium alloys are widely used in the medical industry as replacement materials. These materials may be affected by the conditions and type of environment. In the same manner, soft drinks are widely consumed products. It is of interest for dental industry to know the behavior of medical-grade alloys when these are in contact with soft drinks, since any excessive ion release can suppose a risk for human health. In the present study, the electrochemical behavior of three stainless steel alloys and pure titanium was analyzed using three types of cola soft drinks as electrolyte. The objective of this study was to evaluate the response of these metallic materials in each type of solution (cola standard, light and zero). Different electrochemical techniques were used for the evaluation of the alloys, namely potentiodynamic polarization, linear polarization, and open-circuit potential measurements. The corrosion resistance of the stainless-steel alloys and titanium in the cola soft drinks was provided by the formation of a stable passive film formed by metal oxides. Scanning electron microscopy was used as a complementary technique to reveal corrosion phenomena at the surface of the materials evaluated.

Keywords : Stainless steel, Corrosion, Dental industry, Electrochemical techniques, Soft drinks

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1. Introduction

In recent years, dental replacement industry has shown a growing interest for different kind of materials such as composite resins, metal oxides, glass cements, and metallic alloys [1-3]. Selecting a material for dental applications depends on a number of factors such as corrosion behavior, mechanical properties, cost, availability, biocompatibility, and aesthetics. In this sense, the use of metallic replacement materials is currently widespread since their properties match with the various requirements of dental industry.

Stainless steel and titanium alloys are widely used in medical industry because their biological and anti-corrosive properties [4-6]. For instance, the high corrosion resistance of stainless steel and titanium alloys used in dental devices is based on the formation of a passive oxide film at the metal surface when it is in contact with oxygen from the air, or is immersed in a water-containing media. This passive oxide films may experience dissolution in a strong acid media such as chloride and fluoride-containing products [7-10]. These are usually commercial products such as soft-drinks, toothpastes and mouthwashes. Various studies have shown that in a fluoride-rich acid environment the corrosion resistance of certain metals, especially titanium, is increased [11-13].

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Considering that soft drinks are commonly consumed in the market, it is important to study how these aqueous media behave in contact with dental grade metals such as steel and titanium, since, as a source of metal ions, dental replacement metals can be a risk for human health if any excessive dissolution of metal ion occurs. According to literature data there is no reports regarding the investigation of corrosion behavior of steels and titanium in cola soft drinks, as investigated by electrochemical techniques. Therefore, the aim of this study was contributing to the elucidation of the corrosion mechanisms of the surface of various stainless steels and a titanium metal in the midst of three different commercial cola soft drinks using different electrochemical techniques.

2.1 Materials and methods

metals used in dental industry as materials for dental devices. Samples plates with dimensions of 5×5×5 mm were prepared by grinding using 600 to 1200 grit paper.

Electrochemical studies were carried out in a traditional open air-three electrode cell using saturated calomel as reference electrode and graphite as counter electrode. Three commercially available cola soft-drinks (Coca-Cola company), namely SD-standard, SD-light, and SD-Zero, were used as electrolyte. In order to ensure a good reproducibility of results, the electrochemical cell was heated to 37°C before the starting of each experiment. This temperature was used with aims of recreating corporal conditions. The potential of hydrogen in the solution was measured with a pH-meter (Conductronic pH 120). The metal samples were analyzed by means of scanning electron microscopy (SEM, Hitachi, S-570) before and after the electrochemical tests. All the electrochemical measurements were carried out using a potentiostat/galvanostat (Gamry Interface 1000E).

Potentiodynamic polarization technique was employed to obtain detailed information about anodic branch and corrosion potential of the alloys studied here. The potentiodynamic polarization test was carried out using a scan rate of 60 mV/min. The scans were performed in the potential range of -400 mV to 1000 mV versus the corrosion potential. It's known that materials studied in this work develop a protective oxide layer, in order to evaluate the behavior of these layers, open circuit potential was monitored during 24 hours. Linear polarization resistance (LPR) was used to study corrosion rates at the metal/electrolyte interface of the systems studied in the present work. Linear polarization resistance was acquired from the open circuit region of the polarization scans (~ -20 mV to +20 mV). LPR measurements were

Material	Chemical composition									
	Fe	Cr	Ni	C	Mn	P	S	Mo	Si	Ti
304-H	Bal.	18.0-20.0	8.0-11.0	0.04-0.10	2.00	0.045	0.030		1.00	
310-H	Bal.	24.0-26.0	19.0-22.0	0.04-0.10	2.00	0.045	0.030		1.00	
316-L	Bal.	16.0-18.0	10.0-14.0	0.035	2.00	0.045	0.030	2.00-3.00	1.00	
Titanium Grade 1										99.9

Table 2. Measured pH of the soft-drinks in the present work.

Solution	pH at 15°C	pH at 37°C
SD-Standard	2.69	2.60
SD-Light	3.01	2.88
SD-Zero	3.16	3.06

made during 24 hours.

Electrochemical etching was carried out on all the steels studied to reveal their microstructure. The etching was performed by applying 6 V in an oxalic acid solution (10 g) diluted in distilled water (100 ml) and during 30 seconds of immersion.

3. Results and Discussion

Table 2 shows the pH of the solution at two different temperatures. Interestingly, increasing temperature does not change significantly the pH of the solutions. This is a valuable information with respect to the conditions of the experiments which were then carried out in acidic conditions and simulating the worst of these two cases (corporal temperature).

3.1 Potentiodynamic polarization

The potentiodynamic polarization curves are often useful for the evaluation of the corrosion susceptibility since these provide information about passivation, pitting and rate of corrosion [19].

Fig. 1a shows the potentiodynamic polarization curves of the materials studied in the present work immersed in the SD-Standard solution at 37°C. The titanium metal presented a corrosion potential value of -186.59 mV which is nobler than those corrosion potential values shown for the stainless steels. Among steel samples, the SS-304-H sample displayed the most active behavior with a corrosion potential value of -445.32 mV and a current density value of 0.004618 mA/cm². One can note from the anodic branch of the polarization curves of titanium and SS-316-L samples an active corrosion behavior followed by a passive region. In case of titanium, the active region was defined up to 200 mV, meanwhile this region was limited up to 100 mV in the SS-316-L sample with respect to the corrosion potential. All the steel samples registered an increase in the current density from 400 mV in the anodic branch which is

Fig. 1. Potentiodynamic polarization curves for the stainless steels and titanium in the three types of soft-drinks at 37°C. A) SD-standard solution, B) SD-light solution, C) SD-zero solution.

attributed to the dissolution of the passive film.

Fig. 1b shows the potentiodynamic polarization curves of the samples immersed in the SD-Light solution at 37°C. The polarization curves show a quite similar response of the materials with respect to the results obtained using the SD-standard solution. The titanium metal presented a corrosion potential value of -141.56 mV which is nobler than those corrosion potential values shown for the stainless steels.

The most active behavior was also observed in the SS-304-H sample with a corrosion potential value of -440.03 mV. Interestingly, the highest current density value was obtained in the SS-316-L sample which was one order of magnitude greater than the current density value registered for titanium metal. In fact, wide passive regions were observed in the anodic branch of the titanium, SS-304-H and SS-310-H samples, but not in the SS-316-L sample. In case of titanium, the passive region just started from 266 mV, being preceded for an active corrosion region.

Fig. 1c shows the potentiodynamic polarization curves of the samples immersed in the SD-Zero solution at 37°C. The corrosion behavior of the samples in the SD-Zero solution was also similar with respect to the two solutions presented above. However, the SS-304-H and SS-310-H presented a wide passive region which was attributed to the good stability of the passive film (mainly composed by Cr_2O_3). Meanwhile, the SS-316-L sample displayed a marked active behavior. Table 3 summarizes the electrochemical parameters evaluated from the potentiodynamic polarization curves of the stainless steels and titanium samples.

It is worth noting that SS-304-H and SS-310-H samples had a similar corrosion behavior in all three solutions, presenting wide passive regions (spotted in the anodic branch). Moreover, the appearance of the passive region in these materials was given at current densities smaller than those shown for Ti and SS-

316-L samples. However, the SS-316-L and titanium samples had more positive corrosion potentials and lower current densities than the others steel samples evaluated in the present work.

3.2 Open circuit potential

Fig. 2 shows the open circuit potential (OCP) of the material studied in the present work immersed in the three kinds of cola soft drink solutions at 37°C. Interestingly, the SS-304-H and SS-310-H samples had a significant increase in the OCP within the firsts hours of measurement. Similarly, the SS-316-L and titanium samples also had an increase in the OCP at the beginning of the test, but, in these two cases, it

Fig. 2. Open circuit potential of the stainless-steel alloys and titanium in the three types of cola soft-drinks at 37°C.

Table 3. Parameters calculated from potentiodynamic polarization curves.

Solution	Material	E_{corr} (mV)	I_{corr} (mA/cm ²)	ba	bc
SD-Standard	Titanium	-186.59	0.000331	192.89	246.47
	304-H	-445.32	0.004618	12968.031	71.35
	310-H	-407.17	0.002436	1356.03	57.80
	316-L	-241.28	0.001247	189.17	133.65
SD- Light	Titanium	-141.56	0.00036	170.09	238.22
	304-H	-440.03	0.00379	2433.03	69.68
	310-H	-404.69	0.00214	1448.71	59.64
	316-L	-180.02	0.00404	1356.72	49.84
SD- Zero	Titanium	-171.27	0.00035	189.26	213.80
	304-H	-469.39	0.00394	8416.29	68.63
	310-H	-452.94	0.0036	36478.5	60.05
	316-L	-155.51	0.00073	165.56	151.86

was barely perceptible.

The increase of OCP at the beginning of the test is associated with the formation and growing of a passive film at the sample surface. Overall, all the different materials were stable after 8h.

Gurrappa et al. [20] suggest that a simple way to study the formation of protective films and the passivation of metals in a corrosive environment is monitoring their OCP as a function of time. The increase of the potential in the positive direction indicates the formation of a passive film, and a stable potential indicates that the film remains intact and protective. A potential that fluctuates between the positive and negative sides may indicate that the alloy may not be able to form a stable and protective oxide layer on its surface. A potential drop in the negative direction indicates a rupture, dissolution or non-formation of the protective film. In fact, the potential value itself indicates how good the material is in a given environment. For instance, a high potential in stands indicates a high corrosion resistance. However, when the material has a low potential at rest, the material has either a tendency to oxidize, forming soluble compounds, or the metal forms insoluble products, often oxide layers on the surface that minimizes corrosion [21]. Therefore, even though the SS-316-L steel presented the lowest OCP, it also maintained a very high stability after 10 h in all three types of cola soft drinks. This fact evidences the formation of an insoluble oxide layer at the sample surface which remained intact and protective during the test.

In previous papers [22,23], chromium additions have been found to improve the corrosion resistance of stainless steel remarkably by increasing the stability of the passive layer and decreasing the kinetic of anodic dissolution. According to the results in the present study, the SS-316-L sample displayed the most active behavior due to its lower content of chromium in comparison to the other steel samples evaluated, being in agreement with previous reports.

It is well known that in austenitic stainless steels, chromium is the element responsible for the formation of the passive layer, which is thin and adherent based on Cr_2O_3 oxide, as long as the alloy contains a weight percentage superior than 12% of chromium. This layer provides corrosion resistance to the alloy due to the blockage of oxygen diffusion from the medium into the alloy. In case of titanium, the high corrosion resistance is associated with the formation

of titanium dioxide at the metal surface. According to the results in Fig. 2, this oxide film was also stable during the test. Overall, for dental applications, a material that provides high corrosion resistance are highly valued since, due to the low release of metal ions, they do not affect human health [24].

3.3 Linear polarization

The results of the linear polarization study are presented in Fig. 3. It is observed that, within the first 2 to 4 hours of test, with exception of the SS-316-L, the materials increased their polarization resistance in the three types of cola soft-drinks. This phenomenon is related to the formation of a passive layer which occurred rapidly once material surfaces were in contact with the solution, i.e. it is known that solutions with low pH values may accelerate the formation of passive layers [25]. At the end of the test, it was confirmed that the highest corrosion resistance was obtained for the SS-304-H in the three different types of cola soft drinks. Otherwise, the lower corrosion resistance was presented for the SS-316-L in all three types of soft-drinks. Titanium and SS-310-H samples displayed an intermediate behavior. This behavior can be attributed to the superior content of Ni in the SS-310-H and SS-316-L alloys (19 and 10%, respectively) than in SS-304-H alloy (only 8%) [19].

Previous studies [26] have shown that cola soft drinks promote intensified release of Ni ions ($37.5 \mu\text{g}$) when the composition of the medical-grade alloy is similar to that of stainless-steels (65 Fe, 17 Cr, 12 Ni, 2.5 Mo, 2 Mn, 1 Si, 0.045 P, 0.03 C 0.03 S). In addition to Ni ions, Fe and Cr ions are also prone to

Fig. 3. Polarization resistance of the stainless-steel alloys and titanium in the three types of cola soft-drinks at 37°C.

be released. According to Mikulewicz et al., the greatest mass of released ions corresponded to Fe ions ($\geq 156.1 \mu\text{g}$), followed by Mo ions ($30.12 \mu\text{g}$) and Cr ions ($0.9810 \mu\text{g}$). The lower release of Cr ions with respect to Ni and Fe ions was attributed to the formation of a Cr_2O_3 passive film at the metal surface. These results are very interesting since they reveal that ion release can take place even when the passive film is formed at the metal surface. In fact,

Huang et al. [27] also observed the release of ions when the oxide film was formed in stainless steels. In some cases, oxide films are affected by the conditions of the experiment and may undergo dissolution or damage which can increase ion release. For instance, previous studies have reported that Cr_2O_3 passive films can be affected by mechanical and chemical factors such as intensive wear, contact with toothpaste and immersion in carbonated drinks

Fig. 4. SEM micrographs and elements mapping of Cr(b), Fe(c), Ni(d), Mn(e) and C(f) of the SS-304-H.

Fig. 5. SEM Micrographs and elements mapping of Cr(b), Fe(c), Ni(d), Mn(e) and C(f) of the SS-310-H.

[24]. In the present study, due to the low pH value of the carbonated drink, the passive film underwent dissolution, favoring the release of metal ions, i.e. the stability of the passive film is a function of the pH value [25,28].

Interestingly, the behavior of the Ti sample was not as good as expected which has been attributed to the stability of the passive film in acidic environments. It is well known that Ti alloys present the formation of a TiO_2 passive film which is strongly resistance to corrosion. However, the stability of this passive film is seriously affected when it is immersed in acidic solutions such as artificial saliva solutions (pH 2.5) [27] or carbonated drinks. In the present study, the dependence of the passive film stability on the pH of the solution has promoted the behavior observed in the Ti sample immersed in the cola soft drinks.

3.4 Complementary superficial characterization

Fig. 4a shows the microstructure of the SS-304-H, meanwhile Fig. 4b-f display the elements mapping on the same stainless-steel surface. The elements mapping reveals that voids observed on the steel surface correspond to material removed during metallographic preparation. In addition to this, one can also observe the presence of Mn precipitates on the same sample (see Fig. 4e).

Fig. 5a shows the SEM micrograph of the SS-310-H surface. In this case, the elements mapping in Fig. 5b reveals small areas rich in Cr. To further investigate areas of high Cr concentration, a punctual EDS analysis was performed on one of the Cr rich areas as observed in Fig. 6. The results of the analysis in Fig. 6 revealed that these regions are mainly composed by a high percentage of Cr and C. In this manner, these areas can be associated to chromium carbide precipitates. In fact, previous studies have reported that austenitic stainless steels commonly present M_{23}C_6 precipitates, such as Cr_{23}C_6 principally [29-31]. The microstructure of the SS-316-L is present in Fig. 7, small voids are observed, which correspond to precipitates released during the metallographic preparation.

Fig. 8 shows the SEM micrographs of the titanium and stainless steels after their evaluation in the SD-standard solution at 37°C during 24h. It is observed that all materials evaluated apparently displayed the formation of small voids, these correspond to material removed during metallographic preparation, as

Fig. 6. Closer view of the SS-310-H surface.

Fig. 7. SEM micrographic of microstructure SS-316-L.

Table 4. EDS analysis in the Cr rich areas on the SS-310 H surface.

Element	Weight %	Atomic %
C	17.42	48.33
Cr	57.14	36.62
Fe	21.09	12.58
Ni	4.35	2.47
Totals	100.00	

explained above.

On the other hand, the SS-304-H and SS-310-H alloys presents dark regions, which are attributed to the formation of organic films on the surface of the material, such as carbonates or phosphates of Ca, Na

Fig. 8. SEM micrographs of the stainless-steel alloys and titanium after 24h of tests in the SD-standard solution at 37°C. (red circle = pits, green circle = dark areas).

and K. In a closer study of the dark regions, Fig. 9 shows the elements mapping on the SS-304-H surface. This analysis confirms the presence of an organic film which is mainly composed by C, Na and K.

In addition to the Cr_2O_3 film, extra-organic layers

may also provide protection against corrosion [25]. The result is in agreement with that observed in the electrochemical measurements where the SS-304-H alloy had the highest corrosion resistance and displayed a wide passive region in the polarization studies.

Fig. 9. SEM Micrograph and elements mapping show the elements presents in dark regions in the SS-304-H [C(b), Na(c), K(d) and P(e)].

As mentioned in Section 3.2, the chromium content of the alloy is crucial to improve corrosion resistance. However, due to the presence of precipitates in the microstructure of the SS-316-L alloy, small voids appeared on its surface.

Recent studies carried out on artificial saliva [32] have shown that MnS precipitates or Mo-rich precipitates promote the formation of small voids at the surface of the SS-316-L alloy. These precipitates act as cathodic sites, favoring the corrosion of the metal matrix (Fe-Cr-Ni). Because of the corrosion process, voids like pits appear at the surface of the metal. In the present study, the titanium metal also showed the formation of small voids on its surface.

Fig. 10 shows the SEM micrographs of the titanium and stainless steels after their evaluation in the SD-light solution at 37°C during 24h. Interestingly, the steel samples were less affected by the cola-light soft-drink in comparison to that observed for the same materials in the SD-standard solution. This fact can be attributed to the lower pH value in the SD-standard solution at 37°C. In case of titanium, similar surface characteristics were observed with respect to the sample in SD-standard solution.

Fig. 11 shows the SEM micrographs of the titanium and stainless steels after their evaluation in the SD-Zero solution at 37°C during 24h. It is observed that stainless steels and titanium samples are also less

affected by corrosion in the SD-Zero solution in comparison to the SD-standard solution. Small voids (like-pits) are also observed; however, these voids are in minor quantities than those found in the samples immersed in the other solutions.

Therefore, it is possible to conclude from the present results that materials immersed in SD-standard solution had the highest pitting corrosion phenomena (caused by the precipitate detachment), followed by the metals evaluated in SD-light and SD-Zero solutions. It is worth mentioning that the pH values soft-drinks is usually related to its chemical composition, which may have serious consequences in the corrosion response of alloys [33]. For instance, the main ingredients in cola-drinks are: water, sugar, natural cola extract, phosphoric acid, carbonic acid, caffeine, natural flavors and colorants. Previous reports suggest that corrosion of metals occurs mainly due to a relatively high content of phosphoric acid, carbonic acid, ascorbic acid and sodium citrate [34,35]. In the present study, one of the reasons of the different pH values among the three types of soft-drinks is the content of some components. Previous studies have reported that SD-light drinks (cola drink) have concentrations of 13.7 mg Ca/L; 15.5 mg P/L and 0.31 mg F/L. Otherwise, SD-standard drinks have concentrations of 32.1 mg Ca/L; 18.1 mg P/L and 0.26 mg F/L [36]. Thus, the enhanced corrosion phe-

Fig. 10. SEM micrographs of the stainless-steel alloys and titanium after 24h of tests in the SD-light solution at 37°C.

nomena in the alloys evaluated in the SD-standards solution is the consequence of the chemical composition of the solution, which being more acid accelerates the dissolution of the oxides and in turn promotes the process of corrosion by galvanic pairs caused by the presence of precipitates on the surface of the material.

Several acids such as carbonic acid, phosphoric acid and citric acid are included in soft-drink composition. This mix of acids contributes to reduce the pH value of the drink. The carbonic acid is produced by means of the carbon dioxide in the solution, however, if the carbon dioxide is released from the solution, even so the pH value remains low. The degradation

Fig. 11. SEM micrographs of the stainless-steel alloys and titanium after 24h of tests in the SD-zero solution at 37°C.

of metallic alloys is usually produced for electrochemical reactions within the environment where these are exposed, leading to either a loss of material or the formation of metal oxides [37]. Marcin Mikulewicz et al. [26] have reported a corrosion mechanism based on the formation of a passivation film due

to the spontaneous reaction of the metal surface with air in humid conditions [38]. This passive film is then dissolved due to the protons response in acid solution, leading to the release of a metallic ion. In case of stainless-steels, the ions released are Fe^{3+} , Cr^{3+} y Ni^{2+} . The most significant anodic reactions are pre-

sented as follows:

The acidic pH of carbonated drinks can lead to damage the passive film on the material surface. Previous studies suggest that common corrosion products are likely complex soluble phosphates and insoluble phosphates [39]. In addition, the presence of precipitates on the steels surface promotes the formation of galvanic pairs that accelerate the corrosion process. In this process, the precipitates acts as cathode while the matrix (Fe, Cr and Ni) acts as anode. Once the matrix is dissolved, a void appears on the surface of the metal [32].

4. Conclusions

The corrosion behavior of stainless steel 304-H, 310-H, 316-L and titanium grade 1 (99.9% purity) has been investigated in commercial cola soft drinks. The following conclusions can be made:

(1) The corrosion behavior of the alloys immersed in a soft-drink is closely related to its capacity to form a passive layer which can be stable in that medium. In case of the steels, the best corrosion behavior was presented in that alloys with a higher content of chromium, which is responsible of the formation of a Cr_2O_3 protective film. In a similar way, the titanium presented a good corrosion behavior due to the formation of a TiO_2 oxide layer.

(2) The pH value of the solution (soft-drink) is closely related to its chemical composition, and some of these drinks may result more prone for developing corrosion phenomena because of its low pH values. Although the difference in the pH values of the three types of cola soft-drinks was minimal, it was found that it affects the aggressiveness of the medium, leading to intensify corrosion in the surface of the sample. Intensified corrosion phenomena were observed in the following sequence Standard cola soft drink > Light cola soft drink > Zero cola soft drink.

(3) The presence of precipitates on the stainless steel surface is harmful since these accelerate galvanic corrosion, the precipitates act as cathodes favoring the corrosion of the matrix that acts as anode

and is composed with Fe, Cr and Ni. This process occurs until the precipitates are released, leaving voids on the surface.

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Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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