

## Ion release from non precious dental alloys in the oral cavity

### Liberación de iones de aleaciones dentales no preciosas en la cavidad oral

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#### ABSTRACT

Dental alloys in the oral cavity release ions by corrosive action of saliva, which are deposited in the lower part of the mouth, others diffuse through the gums and most of them pass to the gastrointestinal system. In the present work, nine dental alloys frequently used in our country by people with low resources (316L stainless steel, low and high copper silver amalgams, Co-Cr and Ni-Cr alloys, Cu and Ti-6Al-4V base alloys). Its open circuit corrosion potential was measured, its potentiodynamic polarization curves were plotted and corrosion products were analyzed by EDAX, finding Hg, Ag, Ni, Co, Cu, Zn and Si ions, which can affect the health of users, so it is recommended that dentists and dental technicians inform patients who suffer from hypersensitivity do not use alloys containing potentially allergic metals.

**Keywords:** Corrosion; dental alloys; artificial saliva; corrosion products; polarization curves.

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#### RESUMEN

Las aleaciones dentales en la cavidad oral liberan iones por acción corrosiva de la saliva, los cuales se depositan en la parte inferior de la boca, otros se difunden a través de las encías y la mayor parte pasan al sistema gastrointestinal. En el presente trabajo se sometieron a ensayos de corrosión acelerada en saliva artificial nueve aleaciones dentales de uso frecuente en nuestro país por personas de bajos recursos (acero inoxidable 316L, amalgamas de plata de bajo y alto cobre, aleaciones Co-Cr y Ni-Cr, aleaciones base Cu y Ti-6Al-4V). Se midió su potencial de corrosión a circuito abierto, se trazaron sus curvas de polarización potenciodinámicas y se analizaron por EDAX los productos de corrosión encontrándose iones Hg, Ag, Ni, Co, Cu, Zn y Si, los cuales pueden afectar la salud de los usuarios, por lo que se recomienda a odontólogos y técnicos dentales informar a los pacientes que sufren de hipersensibilidad no usar aleaciones que contengan metales potencialmente alérgicos.

**Palabras clave:** Corrosión; aleaciones dentales; saliva artificial; productos de corrosión; curvas de polarización.

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#### 1. INTRODUCTION

Dental alloys have application in the restoration and correction of lost or deteriorated pieces to preserve the chewing function and the aesthetic appearance; they are used for direct fillings (amalgams), crowns, bridges, inlays, partial or total, fixed or mobile prostheses, implanted structures, or in the form of wires to correct chewing defects using orthodontic appliances [1]. The most traditional are the noble alloys, which contain no less than 75% gold and platinum group metals. These alloys do not deteriorate in their properties over time or lose their aesthetic appearance, but they are excessively expensive [2,3]. For this reason non-precious alloys have been developed, which have been used since the 80s of the last century in developed countries such as the United States and Germany, among these alloys are those of Co-Cr, Ni-Cr, stainless steel and those based on titanium [4–7].

However, to further lower costs and allow access to dental prostheses to sectors of society with low resources and who cannot access the aforementioned alloys, copper based alloys such as Cu-Al, Cu-Ni appeared on the market and Cu-Zn, in the Latin American countries Brazil and Argentina and very little in the United States, as mentioned in international publications [8–13]. In recent years, research has been carried out on individual and

combined non-precious dental alloys in order to evaluate their electrochemical behavior in solutions that simulate natural saliva [14–19]. However, it is necessary to carry out further studies and tests related to the release of metal ions from these alloys in the oral environment and the physiological effects they produce in users.

For these reasons, and given the lack of standards that regulate the use of dental materials in Latin American countries, it is necessary to classify existing alloys in the national and international market, implementing and disseminating techniques to qualify them so that users know their true properties and not those disclosed by the marketing chains. In this work we will determine the open circuit corrosion potentials, corrosion current densities, the polarization curves and we will analyze by EDAX the corrosion products of nine dental alloys (Co-Cr, Ni-Cr, Ti-6Al-4V, alloys Cu base, silver and stainless steel amalgams) in deaerated artificial saliva, assuming that the electrochemical cell acts as an oral cavity, and depending on the type of corrosion product it generates, prevent users from the possible physiological effects to which it would be exposed.

## 2. MATERIALS AND METHODS

### 2.1. Materials

To carry out this work, nine non-precious dental alloys frequently used in our country were selected, the chemical composition of which is shown in Table 1.

### 2.2. Preparation of test pieces

- 316L stainless steel specimens were prepared by cutting pieces of “as-received” wire to expose a surface area of 1 cm<sup>2</sup> to the electrolyte solution.
- High and low copper silver amalgams were crushed and condensed according to the instructions suggested by specialists [22]. In both cases, the specimens were cylinders 0.50 cm high by 1.15 cm in diameter.
- The Co-Cr, Ni-Cr, Cu-Al, Cu-Ni and Cu-Zn specimens were prepared by the lost wax method with an oxygen-butane-propane flame, and by a centrifugation process. The specimens consisted of sheets of 1 cm × 1 cm in surface and 0.5 cm in thickness.
- The Ti-6Al-4V specimens were prepared by cutting 0.50 cm thick pieces of a bar of this “as-received” material, reducing the diameter of said material to 1.15 cm.

### 2.3. Electrolyte

The electrolyte used in the potentiodynamic tests was a previously developed experimental saliva [8,23], which reproduces the electrochemical behavior of natural saliva and whose formula is shown in Table 2. The electrolyte was prepared with deionized water of 18.20 MΩ-cm of electrical resistivity and with analytical grade reagents.

### 2.4. Electrochemical tests

To determine the corrosion products of the alloys under study in artificial saliva, accelerated corrosion tests were carried out, prior to which the corrosion potential of each alloy was measured as follows:

**Table 1:** Chemical composition of dental alloys used in the present work (weight%) [20,21].

ALLOY	TRADENAME	CHEMICAL COMPOSITION (WEIGHT%)
Fe - Cr-Ni-Mn	316L SS	C 0.02 – Cr 17.00 – Ni 12.00 – Mn 1.60 – Si 0.80 – P 0.03 – S 0.02
Cu - Ni	Auro Cast	Cu 57.90 – Ni 22.10 – Al 15.00 – Fe 5.00
Amalgama Alto Cu	Duralloy	Ag 45.00 – Sn 31.00 – Cu 24.000
Cu - Al	Orcast soft	Cu 77.00 – Al 6.50 – Zn 12.50 – Ni 4.50
Cu - Zn	Oropent	Cu 54.10 – Zn 45.70 – Fe 0.05 – Ni 0.02
Amalgama Bajo Cu	Standalloy	Ag 71.00 – Sn 25.70 – Cu 3.30
Ti	Ti-6Al-4V	Ti 89.44 – Al 6.10 – V 4.10 – Fe 0.28 – C 0.08
Co - Cr	Vera PDN	Co 63.50 – Cr 27.00 – Mo 5.50 – Fe 2.00 – Ni 1.00
Ni - Cr	VeraBond	Ni 77.90 – Cr 12.60 – Mo 5.00 – Be 1.90 – Al 2.90

**Table 2:** Chemical composition of the solution used [8,23].

COMPONENT	CONCENTRATION (g/L)
NaCl	0.600
KCl	0.720
CaCl <sub>2</sub> ·2H <sub>2</sub> O	0.220
KH <sub>2</sub> PO <sub>4</sub>	0.680
Na <sub>2</sub> HPO <sub>2</sub> ·12H <sub>2</sub> O	0.856
KSCN	0.060
KHCO <sub>3</sub>	1.500
H <sub>8</sub> C <sub>6</sub> O <sub>7</sub> (Ácido cítrico)	0.030

#### 2.4.1. Corrosion potential measurements

The open circuit corrosion potential was measured with a saturated calomel electrode (SCE) in a three electrode cell with a Princeton Applied Research Model 173 Potentiostat, in the electrolyte solution. Before carrying out the measurement, the solution was degassed with a stream of purified nitrogen for one hour; then the specimen was introduced and an hour was waited for the corrosion potential to stabilize and to take the measurement; This process was repeated 5 times with different specimens and under the same conditions.

#### 2.4.2. Accelerated corrosion tests

Accelerated corrosion tests were carried out in the same cell and with the same potentiostat that was used to measure the corrosion potential, applying the polarization curve technique. The reference electrode was a saturated calomel and the counter electrode a platinum wire coil. The sweep speed was 12 mV<sub>scc</sub>/min controlled with a Universal PAR 175 Programmer and the curves were recorded with an XT PAR model REO 151 plotter. Prior to the beginning of the curves, the corrosion potential was measured in the same way than in section 2.4.1. The anodic curves were drawn in triplicate with different probes from the corrosion potential to 0.200 Vecs above the rupture potential, and the cathodic curves were also drawn from the corrosion potential to a negative potential sufficient to apply the Tafel slopes. After the anodic tests, the specimens were dried with hot air and carefully disassembled to later analyze the corrosion products.

#### 2.5. Corrosion product analysis

The corrosion products generated on the specimens were analyzed by the X-ray Energy Dispersive Spectrum Method (EDS or EDXS) [24]. Said method consists of analyzing the characteristic X-rays emitted by the sample reached by a high-energy electron beam from a scanning electron microscope, allowing the identification of the elements that make up said sample through a multichannel analyzer.

The main advantage of EDAX microanalysis is the small volume of material it analyzes, usually on the order of one cubic micron. Another advantage is that the analysis is non-destructive so that the sample can continue to be analyzed by other complementary techniques. This system allows the simultaneous determination of all the elements present in the volume of material analyzed from Z = 10 with Si (Li) detectors coupled to a scanning electron microscope.

To determine the corrosion products in this work, the Philips SEM 500 scanning electron microscope was used, from the Electron Microscopy Laboratory of the CNEA Materials Department (Buenos Aires-Argentina), to which an energy dispersive detector is attached. X-ray, whose minimum detection volume is approximately one cubic micron, consistent with the detection capacity of the EDS method discussed above.

### 3. RESULTS AND DISCUSSION

#### 3.1. Open circuit corrosion potentials

Table 3 shows the average open circuit corrosion potentials and the error made in the measurement, ordered from the noblest to the most active, forming a galvanic series in aerated artificial saliva. 316L stainless steel has the noblest electrode potential of all the dental alloys considered in this work ( $-0.198 V_{scc}$ ). Its high resistance to

**Table 3:** Corrosion potentials of dental alloys in artificial saliva.

ALLOYS	TRADENAME	$V_{\text{corr}} (V_{\text{sce}})$	$I_{\text{corr}} (\mu\text{A}/\text{cm}^2)$
Fe – Cr	316L SS	$-0.198 \pm 0.007$	0.220
Cu – Ni	Aurocast	$-0.287 \pm 0.008$	4.270
High Cooper Amalgam	Duralloy S	$-0.346 \pm 0.010$	0.140
Cu – Al	Orcast soft	$-0.370 \pm 0.005$	2.840
Titanium base alloy	Ti-6Al-4V	$-0.402 \pm 0.008$	1.460
Ni – Cr – Mo	Verabond	$-0.450 \pm 0.012$	2.740
Cu – Zn	Oropent	$-0.524 \pm 0.017$	0.050
Co – Cr	Vera PDN	$-0.591 \pm 0.010$	0.590
Low Cooper Amalgam	Standalloy F	$-0.625 \pm 0.012$	0.120

corrosion is due to its high Cr content (between 16 and 18 %) and its biocompatibility makes it a useful material for medical applications, orthopedic implants and orthodontic braces [6,25].

The corrosion potentials of high and low copper silver amalgams (Duralloy and Standalloy) are:  $-0.346 V_{\text{sce}}$  and  $-0.625 V_{\text{sce}}$  respectively. These values are related to the high copper content (24 %) of Duralloy and the low content of this metal in Standalloy (3.30 %), which makes it more vulnerable to corrosive attack.

Copper base alloys have a wide range of open circuit corrosion potentials from  $-0.287 V_{\text{sce}}$  to  $-0.524 V_{\text{sce}}$ . The high corrosion potential of the Cu-Ni alloy is due to its high content of Cu and Ni; On the other hand, the low potential for open circuit corrosion of the Cu-Zn alloy is due to its high Zn content (approximately 45 %). The intermediate value of the corrosion potential of the Cu-Al alloy is attributed to the high content of Cu and low content of Zn and Ni.

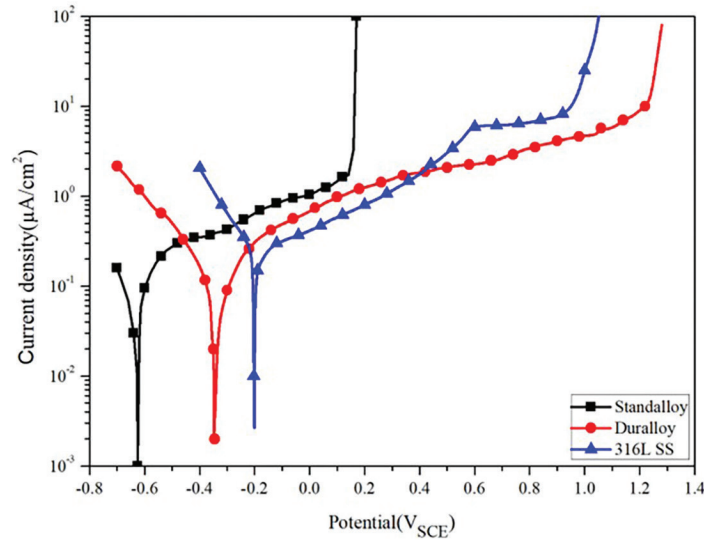
The Co-Cr alloy has a low corrosion potential,  $-0.591 V_{\text{sce}}$ . On the other hand, the corrosion potential of the Ni-Cr alloy is higher,  $-0.450 V_{\text{sce}}$ , agreeing in both cases with its chemical composition, that is, considerable amounts of Co, Ni and Cr, contained in these alloys whose electrode potentials they are very low. These alloys are used in orthopedic implants and to fabricate removable partial denture metal frameworks. At present, CoCr alloys are used as metallic substructures for the fabrication of porcelain-fused-on-metal restorations [26].

Ti-6Al-4V alloy has low electrode potential,  $-0.402 V_{\text{sce}}$ . This alloy is very reactive, its high resistance to corrosion is due to the titanium oxide ( $\text{TiO}_2$ ) that forms rapidly on its surface, making it as resistant as a noble metal. It is a biocompatible and osseointegrable material, which is why it is used in dental and orthopedic implants [3,7,18].

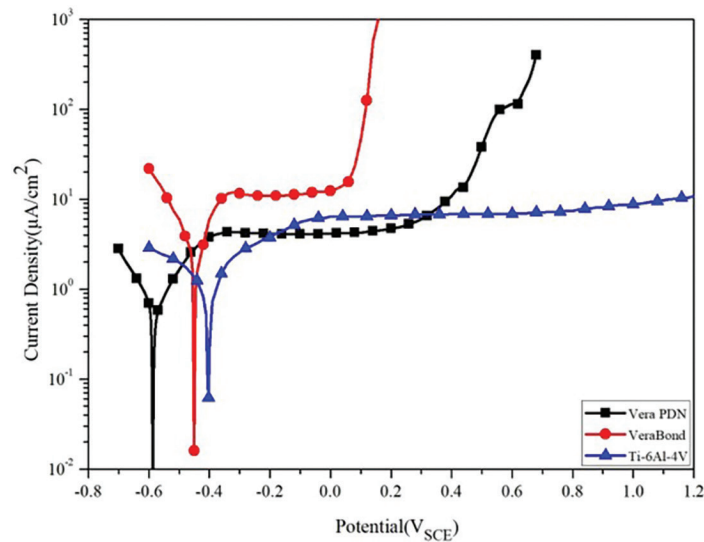
### 3.2. Polarization curves

The polarization curves in artificial saliva were determined under static hydrodynamic conditions at room temperature. Although the oral temperature is 37 °C, it was observed through previous tests that there are no significant differences in the electrochemical behavior of dental materials between room temperature (25 °C) and the temperature of the mouth.

Figure 1 shows the anodic polarization curves for 316L stainless steel and silver amalgams. The passive zone of 316L stainless steel extends from its corrosion potential to  $0.920 V_{\text{sce}}$  and the current density in the passive zone increases from  $0.220 \mu\text{A}/\text{cm}^2$  to  $8.100 \mu\text{A}/\text{cm}^2$ . In this material from  $1 V_{\text{sce}}$ , increases in the corrosion current density are observed due to the decomposition of the solution. Low copper amalgam (Standalloy) has a passive zone that extends from its corrosion potential to  $0.120 V_{\text{sce}}$  and a current density that increases from  $0.120 \mu\text{A}/\text{cm}^2$  to  $1.600 \mu\text{A}/\text{cm}^2$ ; from this value the current density increases rapidly due to the dissolution of the phase  $\gamma_2$ , by de-alloying and / or pitting of the amalgam. High copper amalgam (Duralloy) has a passive zone that also extends from its corrosion potential up to  $1.140 V_{\text{sce}}$  and a current density in this zone that slowly increases from  $0.140 \mu\text{A}/\text{cm}^2$  to  $7.024 \mu\text{A}/\text{cm}^2$ ; From this value the current density increases rapidly due to the growth of the corrosion product layer and the decomposition of the solution when reaching the oxygen evolution potential. It is also observed that the corrosion potentials differ by less than  $0.280 V_{\text{sce}}$ , the least noble or most active being the low copper amalgam.



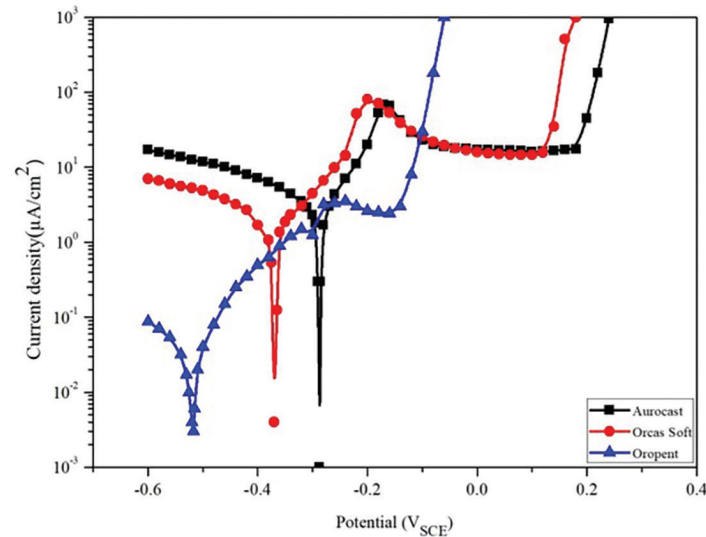
**Figure 1:** Potentiodynamic polarization curves of 316L stainless steel, and high and low copper silver amalgams (Duralloy and Standalloy).



**Figure 2:** Potentiodynamic polarization curves of Vera PDN (Co-Cr), VeraBond (Ni-Cr) and Ti-6Al-4V.

The polarization curves of the dental alloys Vera PDN (Co-Cr), VeraBond (Ni-Cr) and Ti 6Al 4V are shown in Figure 2. The passive zone of the Vera PDN alloy extends from  $0.340 V_{scc}$  to  $0.320 V_{scc}$ . From this value the current density increases rapidly due to the dissolution of the interdendritic zone due to the presence of precipitates. The passivation current density is of the order of  $4 \mu A/cm^2$ . The passive zone of the VeraBond extends from  $0.320 V_{scc}$  to  $0.030 V_{scc}$  and the passivation current density is  $11 \mu A/cm^2$ . From this potential as in the previous case, the current density increases rapidly due to the dissolution of the interdendritic zone due to the presence of Cr and Mo (mainly Mo) precipitates [27,28]. The passive zone of Ti-6Al-4V extends from  $-0.340 V_{scc}$  to potentials above  $1.200 V_{scc}$  with an average passivation current density of  $7 \mu A/cm^2$ . The dissolution of the passivating oxide film ( $TiO_2$ ) is manifested by the increase in the current density and by the start of a mincing process on the surface of the specimens, a process that is accompanied by the evolution of oxygen, as it was reported by Speck and Franker [29].

The polarization curves of the copper based alloys are shown in Figure 3. The Auocast alloy has a wide passive zone that extends from  $-0.140 V_{scc}$  to  $0.180 V_{scc}$  with a current density of  $16 \mu A/cm^2$  in that zone. The Orcast Soft has a passive zone that extends from  $-0.140 V_{scc}$  to  $0.120 V_{scc}$  with a passivation current density of  $16 \mu A/cm^2$ . Oropent's passive zone extends from  $-0.240 V_{scc}$  to  $-0.150 V_{scc}$  with a current density of  $2.70 \mu A/cm^2$ .



**Figure 3:** Potentiodynamic polarization curves of Aurocast (Cu-Ni), OrcaSoft (Cu-Al) and Oroperent (Cu-Zn).

From the breaking potentials, similar to the Vera PDN and VeraBond alloys, the current density increases rapidly due to the dissolution of the interdendritic zone formed by the segregation of Fe and Ni and insoluble in the  $\alpha$  phase [30].

### 3.3. Corrosion current densities

The corrosion current densities of the alloys under study were determined using the Tafel slope method, whose values are shown in Table 3. These results were obtained from the polarization curves of the dental alloys shown in the figures 1 to 3:

- Low copper amalgam (Standalloy) has a corrosion current density of  $0.120 \mu\text{A}/\text{cm}^2$  and a very short passive zone. For the breakdown potential of this amalgam ( $0.120 \text{V}_{\text{SCE}}$ ), the corrosion current density is  $1.600 \mu\text{A}/\text{cm}^2$ ; which is much lower than that of 316L stainless steel and high copper silver amalgam (Duralloy), whose values at their breakdown potentials are 8 and  $7 \mu\text{A}/\text{cm}^2$  respectively, as can be seen in figure 1. However, at potentials slightly greater than Standalloy breakdown potential, the current density increases rapidly, deteriorating the amalgam.
- Table 3 shows that of the dental alloys Vera PDN, VeraBond and Ti-6Al-4V, the noblest is the Ti alloy. This alloy has a corrosion current density of  $1.460 \mu\text{A}/\text{cm}^2$ , a greater passive zone than VeraBond and Vera PDN as seen in Figure 2. At potentials higher than the breakdown potentials of Vera PDN (Co-Cr) alloys and VeraBond (Ni-Cr), the current density of the Ti6Al4V alloy is  $7 \mu\text{A}/\text{cm}^2$  while the alloys referred to above begin to deteriorate due to the effect of the accelerated corrosion of the electrolytic medium.
- In copper based alloys, the least active is Oroperent whose corrosion current density is  $0.050 \mu\text{A}/\text{cm}^2$ , followed by OrcaSoft and then Aurocast with 2.840 and  $4.270 \mu\text{A}/\text{cm}^2$  as shown in table 3. The passive zone of OrcaSoft is greater than the passive zone of Oroperent and less than Aurocast, as seen in Figure 3. At the breakdown potential of OrcaSoft its corrosion current density is  $35 \mu\text{A}/\text{cm}^2$ , that of Aurocast  $21 \mu\text{A}/\text{cm}^2$  and Oroperent greater than  $1000 \mu\text{A}/\text{cm}^2$ .
- At high potentials, greater than  $1 \text{V}_{\text{SCE}}$ , the corrosion current densities of high copper amalgam (Duralloy), 316L stainless steel and Ti-6Al-4V are 19, 24 and  $8 \mu\text{A}/\text{cm}^2$  respectively. In other words, the most corrosion-resistant alloy in the oral environment is Ti6Al4V, which is why it is recommended for use in implants and dental and orthopedic prostheses.

### 3.4. Corrosion products

Corrosion products and EDAX spectra of low and high copper amalgams are shown in Figures 4 and 5 respectively. The highest peaks correspond to Hg and Ag and the smallest to Sn and Cu, in agreement with the results of other investigators [31,32]. Since oxygen and hydrogen are not determined by this method, it is assumed that oxides and hydroxides are formed with these elements. The  $\text{OH}^-$  ions are formed by the reduction of  $\text{O}_2$ , while the  $\text{Ag}^+$  and  $\text{Sn}^{++}$  ions come from the dissolution of the amalgam.

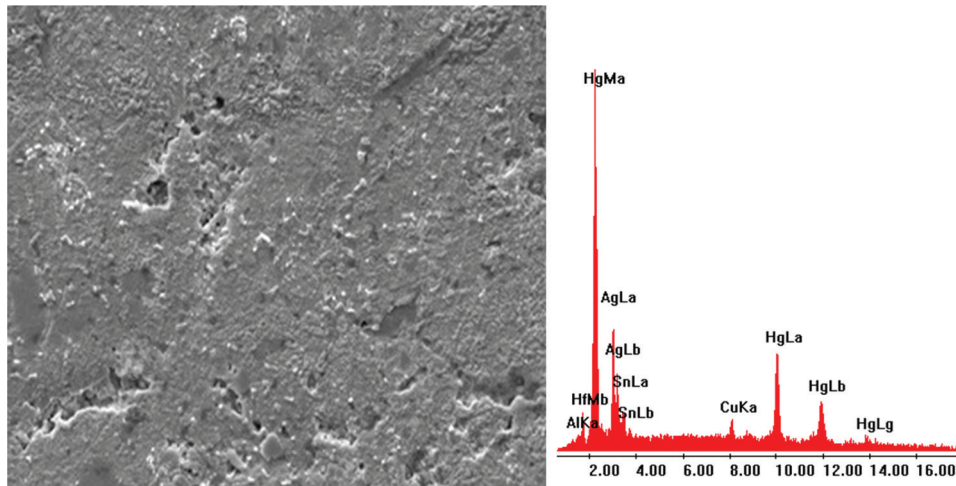


Figure 4: Micrograph of corrosion products and EDAX on Standalloy (1440 ×).

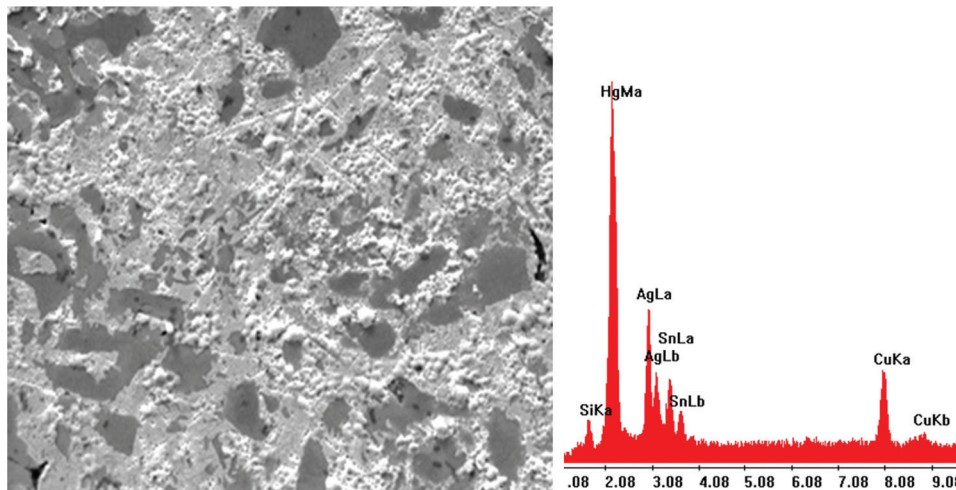


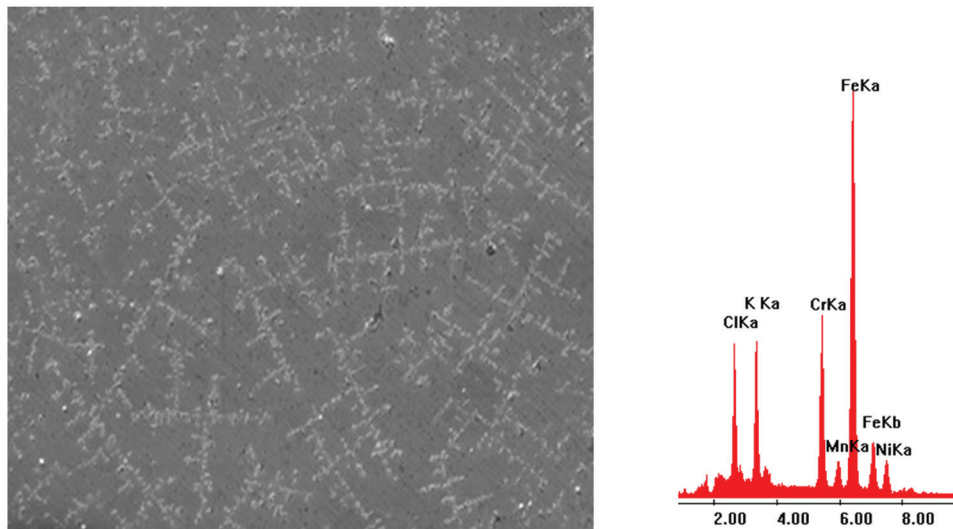
Figure 5: Micrograph of corrosion products and EDAX on Duralloy (1600 ×).

In dissolving amalgams, when a discontinuous film forms on the surface, some pores can be closed by the formation of insoluble products such as tin and silver oxides. Oxides can be formed as follows [33]:

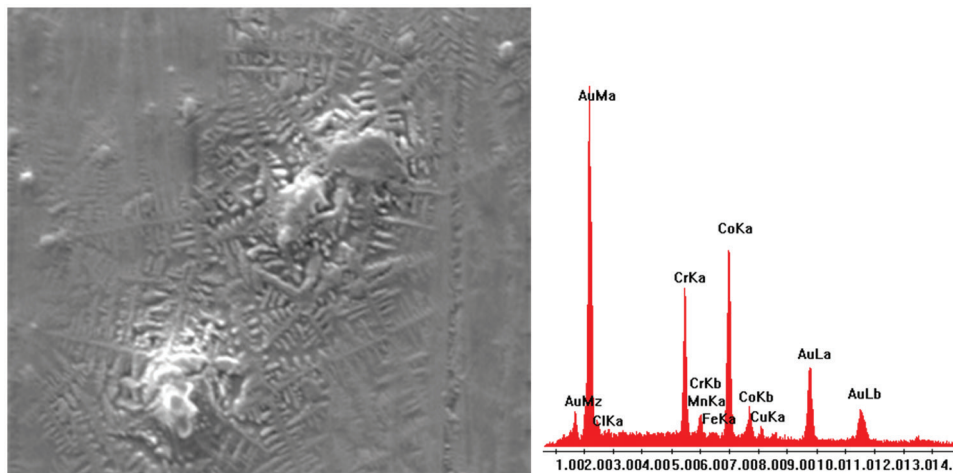


The  $\text{Cl}^-$  ions found in the electrolytic solution are capable of forming with the components of amalgams, Ag, Sn and Zn, according to Mueller [34], the following compounds: zinc chloride ( $\text{ZnCl}$ ), stannous chloride ( $\text{SnCl}_2$ ), stannic chloride ( $\text{SnCl}_4$ ), SnCl compounds such as the hydrated  $\text{Sn}(\text{OH})\text{Cl} \cdot \text{H}_2\text{O}$  and  $\text{Sn}_4(\text{OH})_6\text{Cl}_2$ , copper chloride ( $\text{CuCl}$ ), cupric chloride ( $\text{CuCl}_2$ ), complex hydrated cupric chloride [ $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ ] and silver chloride  $\text{AgCl}$ . According to Craig R.G, referenced by Fathi and Mortazavi [35], the following products have been identified in patient amalgams:  $\text{SnO}$ ,  $\text{SnO}_2$ ,  $\text{Sn}_4(\text{OH})_6\text{Cl}_2$ ,  $\text{Cu}_2\text{O}$ ,  $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ ,  $\text{CuCl}$ ,  $\text{CuSCN}$  and  $\text{AgSCN}$ .

Figure 6 shows the corrosion products and the EDAX spectrum of 316L stainless steel. Large peaks of Fe and Cr, and small peaks of Mn and Ni are observed in the spectrum. The peaks of Cl, P and K correspond to the components of the electrolyte solution. As this technique does not detect oxygen and hydrogen, it is reasonable to assume that the products formed are oxides, hydroxides, phosphates and carbonates of the mentioned metals. Iron in corrosion produces ferric ions ( $\text{Fe}^{3+}$ ), ferric hydroxide ( $\text{Fe}(\text{OH})_3$ ) and ferrous hydroxide ( $\text{Fe}(\text{OH})_2$ ), rust



**Figure 6:** Micrograph of corrosion products and EDAX on 316L stainless steel (260 ×).



**Figure 7:** Micrograph of corrosion products and EDAX on Vera PDN (2880 ×).

$\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$  and dry corrosion products such as black ferrous oxide ( $\text{FeO}$ ), black magnetite ( $\text{Fe}_3\text{O}_4$ ) or red, brown hematite ( $\text{Fe}_2\text{O}_3$ ) [36]. The release of metal ions from stainless steel orthodontic wires and accessories mainly involves iron, chromium, nickel and their corrosion products. They can be adsorbed by enamel or transferred to the gastrointestinal tract during ingestion of food [37].

Figure 7 shows the corrosion products and the EDAX spectrum on the Co-Cr alloy, observing high peaks of Co and Cr and smaller peaks of Mn, Fe and Cu. This leads to the conclusion that oxides and hydroxides of these elements such as  $\text{Cr}_2\text{O}_3$ ,  $\text{MoO}_3$  or nickel were formed, which confer good properties against corrosion, which are brittle as oxides [28].

The corrosion products and EDAX on the Ni-Cr alloy are shown in Figure 8 in which large peaks of Ni and Cr are observed, and small peaks of P, Cl, K, Fe and S. It is expected that the compounds that are formed are oxides, hydroxides, chlorides and phosphates of the metallic elements [15]. On the other hand, in the spectra it is observed that the Ni-Cr alloy (VeraBond) releases a greater amount of ions than the Co-Cr alloy (Vera PDN) in the electrolytic medium, these ions being the ones that can cause allergenic problems associated with nickel.

The corrosion products and the EDAX spectrum of the Cu-Al, Cu-Ni and Cu-Zn alloy are shown in Figure 9, 10 and 11 respectively. High peaks corresponding to Cu and small peaks of Zn, Ni and Fe are observed. The peaks corresponding to K, Cl, P and Ca are due to the composition of the solution. Likewise, as it is not possible to detect oxygen and hydrogen by this method, it is expected that oxides and hydroxides are formed with these elements, iron and nickel phosphates and chlorides in minority form and probably copper thiocyanate [14].



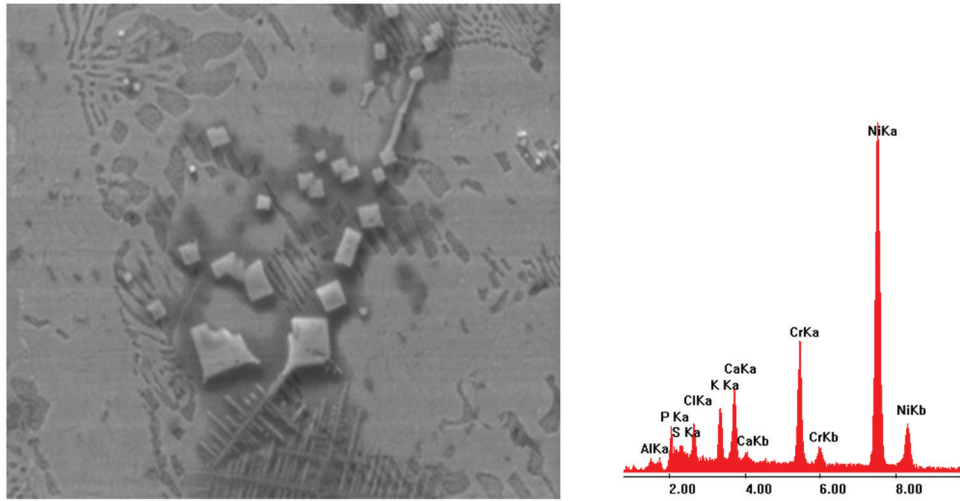


Figure 8: Micrograph of corrosion products and EDAX on VeraBond (1600 ×).

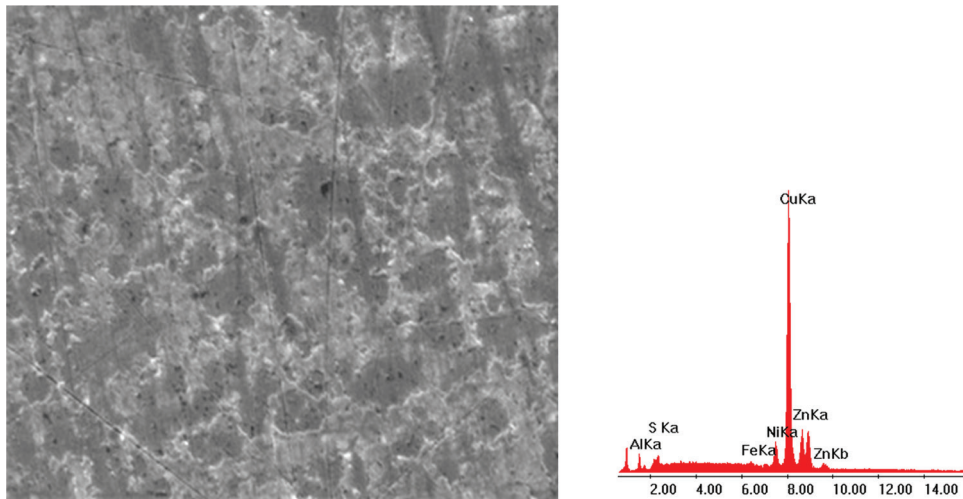


Figure 9: Micrograph of corrosion products and EDAX on Orcast Soft (1440 ×).

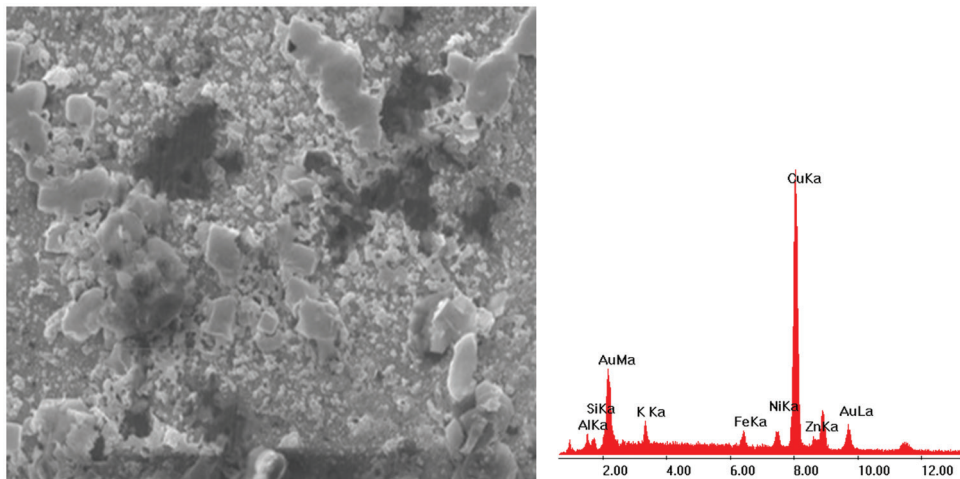
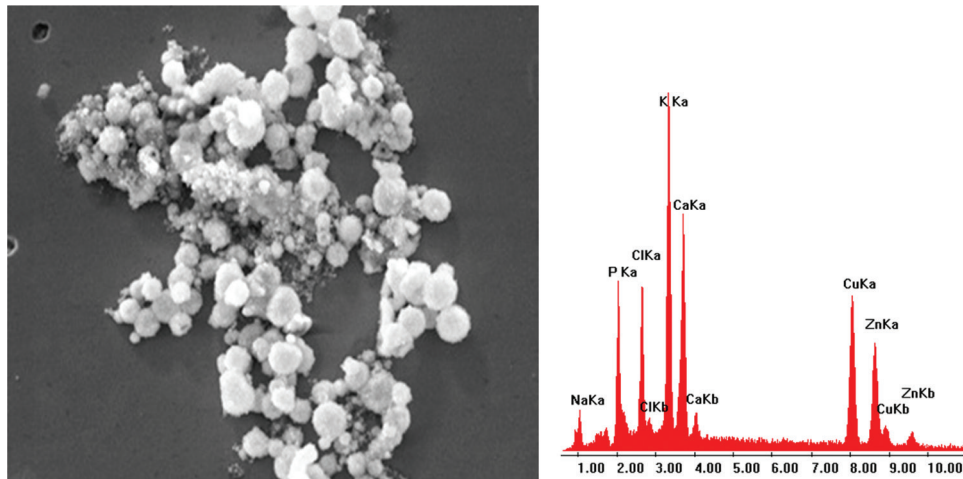
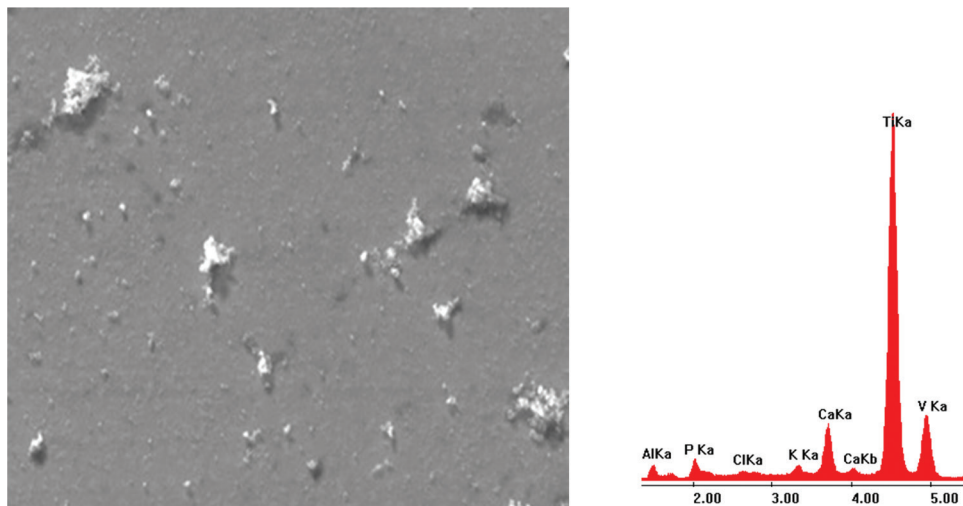


Figure 10: Micrograph of corrosion products and EDAX on Aurocast (1120 ×).



**Figure 11:** Micrograph of corrosion products and EDAX on Oroperent (560 ×).



**Figure 12:** Micrograph of corrosion products and EDAX on Ti-6Al-4V (640 ×).

The corrosion and EDAX products on the Ti-6Al-4V alloy are shown in Figure 12. The spectrum shows a high peak of Ti and small peaks of V and Al, so we must assume that titanium oxides are formed, aluminum and vanadium; the most common are  $\text{TiO}$ ,  $\text{TiO}_2$  and  $\text{Ti}_2\text{O}_3$ ;  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  are resistant to corrosion. The most used is  $\text{TiO}_2$  for its stability, according to bibliographic information [38], in a millisecond, a layer of 10 Å (one nanometer) of oxide is formed that in one minute will become a layer of 100 Å (10 nanometers) when the metal is exposed to an oxygen environment.

### 3.5. Biological implications of corrosion products

The corrosion products of the alloys under study and the ions released into the environment form the corrosion products and remain stored in the oral mucosa in the form of staining or pass through the digestive tract to the stomach. Part of them are eliminated abroad and the rest is stored in an organ such as the liver, kidneys, lungs and brain [39,40]. Next, and having detected that all the metals used in the manufacture of dental alloys are released to a greater or lesser degree to the biological environment, a brief review of the effects caused by them will be made:

- The main component mercury of amalgams is a toxic metal both in its elemental form and in its organic and inorganic derivatives. As a simple metal, it is poorly soluble and therefore not very toxic when ingested. However, the fact of emitting vapors at any temperature makes it very dangerous, leading to acute and chronic poisoning by inhalation of these vapors. Mercurial salts are very active poisons, the more so the greater their solubility. Calomel are low toxic inorganic mercurous salts, as they are insoluble, but within the body they can be transformed into mercurous chloride, which is a powerful toxic. Mercury is very permeable through the

cell membrane and can pass from the gastrointestinal tract to the lungs and brain. Several investigators have reported the correlation between the number of amalgam fillings and the concentration of mercury in blood plasma, urine, feces, saliva, and different organs such as the pituitary gland [41,42]. Oral lesions from mercury poisoning consist of swelling and redness of the gums and tongue, erosions and ulcerations of the palatal, gingival, and lingual mucosa, as well as tooth loss associated with very aggressive necrotizing gingivitis [39,40].

Silver, which is another major component of amalgam, produces pigmentation in the mucous membranes when its exposure is prolonged. This pigmentation is due to the reduction of the silver compound in the tissues giving a bluish gray appearance. Pigmentation in the oral mucosa extends throughout the cavity. The lingual beds are also impregnated and silver amalgam tattooing on the buccal mucosa is common in dental practice [43].

- Co-Cr, Ni-Cr alloys and stainless steels release Ni, Cr and Co ions into the electrolyte solution which form oxides, hydroxides, chlorides and phosphates, some of which are toxic to health. Nickel is a potential allergen, highly sensitizing and the most common cause of allergic contact dermatitis, it is present in jewelry and household utensils. Therefore, it can be considered a health hazard increasing with the use of dental restorations. Ni ions produce nonspecific allergies and inflammations around restorations that can adopt lichenoid and sometimes erosive reactions, with women being more hypersensitive to this metal, probably because they are in contact with Ni from an early age through the jewelry and utensils they wear [44,45].

Chromium is less sensitizing than nickel. It forms oxides, but the only ion absorbed intracellularly by red blood cells is  $\text{Cr}^{6+}$ , which is then converted into  $\text{Cr}^{3+}$ ; This ion participates in essential processes for the survival of the cell and is required in the normal metabolism of carbohydrates and lipids, as well as in the stabilization of proteins and nucleic acids. In contrast,  $\text{Cr}^{6+}$  has a high capacity to cause diseases in the workplace, including some types of cancer in exposed people [46]. On the other hand, although the alloys mentioned above contain between 11% and 35% chromium, allergies are rarely observed. It is less of a problem than nickel allergy, however, dentists should warn users.

Cobalt is much less sensitizing than Cr. However, an overdose of cobalt decreases the activity of the thyroid gland, increases the number of erythrocytes in the blood, temporarily dilates blood vessels, decreases the ability of the blood to clot, and it may be the cause of cardiomyopathies [47]. Exposure to Co and Cr occurs mainly through three routes, namely inhalation, ingestion, and skin contact. In the present case, these metals are also in contact with the mucosa of the mouth; They have beneficial effects on human health, but they also have harmful effects. Metals such as beryllium, cadmium and chromium (VI) are considered carcinogens by the US National Toxicology Program and among the probable carcinogens is Co [48].

- The ions of Cu, Al, Zn, and Fe released into the solution, as the copper-based alloys dissolve, form oxides, hydroxides, chlorides and phosphates which are stored in the gingival tissue adjacent to the restored tooth. These ions affect the viability and proliferation of lymphocytes. Over time, the concentration of copper increases in the gums, causing inflammation, alteration of cellular immunity and oral homeostasis. In general, these ions contribute to a variety of immunopathological conditions including periodontal diseases and decreased resistance to oral infections [33].

Copper, which is the majority element in Cu base alloys, plays an important role in metabolism. An adult man who contains in his body from 100 to 150 mg of this element needs 2 mg of copper per day. The lack of copper in the diet can cause anemia, diarrhea and nervous disorders. In contrast, excessive ingestion of compounds such as copper sulfate can cause vomiting, falls, seizures, or death itself [49].

The aluminum contained in the alloys Cu-Al, Cu-Ni and Ti-6Al-4V is a metal that is present in water, food and air. Apparently it is a harmless element for the human body. Regarding its toxicity, prolonged inhalation of this metal dust can cause lung irritation or fibrosis. Exposure to aluminum can cause alterations in various organs (kidneys, bones and central nervous system). Thus, it has been related to Alzheimer's (in the absence of another causative agent), Parkinson's diseases, and neuro-behavioral disorders [50]. Aluminum replaces the Ca in bones and makes them brittle. On the other hand, it causes conditions in dialysis patients due to their renal inability to eliminate aluminum [51].

Zinc is a toxic metal. Acute symptoms of poisoning by this element are accompanied by chills, fever, sweating, tachycardia, nausea, and vomiting. They produce dryness of the upper respiratory tract. The teeth can loosen due to destruction of the periodontal tissues, although this does not cause great pain. On the other hand, research carried out in recent years has shown that zinc does not significantly increase serum levels in recurrent aphthous stomatitis (RAS) [52], understood as the presence of painful oval ulcers or erosions, generally located in the loose oral mucosa of the lips, cheeks and tongue, surrounded by an erythematous halo.

- The release of Ti, Al and V ions from the Ti-6Al-4V alloy to the solution produces titanium and aluminum oxide on the surface of the alloy. The vanadium species that predominate under physiological conditions and are biologically important are the ions, +3, +4, and +5 [53].

Titanium is a material that has been used in implants since the 1970s for its excellent biocompatibility properties. However, there are reports of adverse side reactions in the health of these patients. Some symptoms of TiO<sub>2</sub> (Ti oxide) lie in [54]:

1. Metallic taste (in the presence of intraoral amalgam and gold) due to oral galvanism.
2. Increased corrosion of titanium in the presence of fluoride-containing toothpastes and gels.
3. Some people react with gastrointestinal symptoms.

Titanium oxide is also found in some dental materials such as composite resins, endodontic canal filling cements, and as a coloring agent [54]. The Ti - 6Al - 4V alloy used in trauma applications has a high level of biocompatibility and corrosion resistance, while offering advantages for diagnostic imaging [55]. This alloy contains aluminum and vanadium which are toxic metals. Vanadium toxicity acts on the liver, kidneys, inhibits enzymes, affects DNA and does not allow the synthesis of fatty acids [53, 56].

#### 4. CONCLUSIONS

From the results obtained in this work, the following conclusions are deduced:

1. All dental alloys dissolve in artificial saliva, the most noble being 316 L stainless steel, the least noble being silver amalgam with low copper content, and the Ti - 6Al - 4V alloy being the most resistant to corrosion because it has a passive zone extending from the corrosion potential down to 1.2 V<sub>sce</sub>.
2. High copper silver amalgam has a more noble open circuit corrosion potential than Ni-Cr, Co-Cr, Cu-Al, Cu-Zn and Ti-6Al-4V alloys.
3. People with an allergic predisposition should not use alloys containing potentially allergic metals such as nickel and chromium to avoid hypersensitivity problems.
4. Dentists and dental technicians must inform patients of the biological effect produced by the release of ions from each of the alloys used in dental restoration.

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