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Corrosion of Biomaterials Used in Dental Reconstruction Dentistry

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1. Introduction

Biocompatibility is a complex concept that takes into account all the processes occurring in the interaction between the biomaterial and a living organism. The biocompatibility means the property of a material to be compatible with living organism, that to be accepted a definitive manner by body without causing side effects and without chemical or mechanical damage [11, 47, 49].

Corrosion of biomaterials used in dentistry is the process of altering or destroying such materials in interaction with the oral environment [10]. Generally, all dental materials are subjected to the aggressiveness in the oral environment, in a certain period of time, longer or shorter, they shall chemically degrade. The term degradation of biomaterials in a biological environment combines metallic biomaterials corrosion or damage of ceramic and polymeric biomaterials with the host tissue reaction [11].

Oral environment is considered a highly chemical aggressive environment, characterized by frequent and important pH modifications due to various types of food or microbial flora. In this environment, dental materials can be dissolved in water or saliva or they can release constituents by the diffusion processes, they can be eroded in the presence of acids, they can change colour, or corrode.

Metallic biomaterials are a class of materials recommended for dental applications due to their very good mechanical properties and an acceptable biocompatibility. Metals and alloys commonly used as biomaterials are gold (Au), cobalt-chrome alloys (CoCr), austenitic stainless steel (316L), titanium and titanium alloys (TiNi, Ti-6Al-4V) and silver-mercury alloys (AgHg). Pure metals are seldom used, their alloys being mostly used due to the fact that by alloying, they enhance certain properties such as corrosion resistance and hardness. (e.g. pure gold,

although biologically inert, it has poor mechanical properties, on the other hand, steels, which have excellent mechanical properties do not show a good corrosion resistance).

Titanium is a material reactive in water, air, or any other electrolyte where it covers spontaneously with a titanium oxide layer. It is considered an inert material, as in contact with the tissue, it is rapidly inactivated forming on its surface a thin, hard, and protective layer of oxide, in less than one second [9, 10, 11, 47]. The titanium oxide film formed spontaneously is continuously regenerating and it provides an in-depth protection for the metal towards chemical attack, including the aggressive attack produced by the liquids of the body. Titanium is still considered the ideal material in endosseous dental implant. It does not produce any magnetic effect, it does not produce any magnetic field to disturb the activity around the cells; oxides from the surface of the implant being very adherent and insoluble, and they prevent the release and direct contact between the potentially harmful metal ions and tissues (biological compatibility). Titanium does not produce organic-metallic compounds, which are toxic, or if they are produced, such organic-metallic are unstable. Surface of oxides, consisting of TiO , TiO_2 , Ti_2O_3 , and Ti_3O_4 attracts and binds biomolecules (Kasemo 1983). The major disadvantage of this metal is the difficulty to cast it. Today it is obtained by dissociation in vacuum at 1400°C having a purity of 99.85 to 99.95%. Titanium alloys are better tolerated than pure titanium because the oxide layer that forms is higher (of approx. 10-20 μm) [9, 10]. Recent researches have demonstrated that the oxide layer (TiO) considered so stable regenerates every nanosecond, and re-oxidation is a major advantage due to minimizing the risk of biodegradation. It has been proven that next to resistance to corrosion, biological compatibility, resistance and price, the alloys used in medicine are "conversion" alloys based on titanium. Resistance to corrosion can be increased by alloying with molybdenum, zirconium, rhenium, niobium, chromium, manganese. Biomedical titanium alloys are: Ti-Al-V, Ti-Al-Mo, Ti-Al-Cr, Ti-Al-Cr-Co. Frequent use of titanium alloy Ti-6Al-4V for implants is determined by a combination of the most numerous and more favourable characteristics, which include resistance to corrosion, durability, low elasticity module and the ability to adhere with bone and other tissues (osseointegration) [13, 14, 18, 20, 36]. However, there are a number of issues related to the effects the components of the alloy can have. Aluminium and vanadium are elements released into the tissue. Therefore, a number of titanium alloys have investigated (Ti-Al-Nb, Ti-Zr-Al) and it was demonstrated that the Ti-6Al-6Nb alloy has properties comparable to the Ti-6Al-4V alloy, but it shows a greater strength and resistance to corrosion [53, 55]. Analysis of possible reactions to prolonged contact of living tissues with the alloying elements of titanium alloys showed that the use of titanium alloys containing large amounts of vanadium, cobalt and nickel is not recommended. On the other hand, introducing the alloying elements into the titanium alloys such as molybdenum, niobium, zirconium, and tantalum is not limited quantitatively. They increase the anticorrosive resistance, facilitate the increase of strength and they are compatible with living tissues. The content of aluminium and vanadium must not exceed 6%, and the content of Fe, Cr, Mn, and Ni is of 1% [23, 46,47,48].

Release of vanadium ions in the body can produce serious damages to the respiratory system and of the blood plaquettes producing systems, but it is a long process. However, it is taken into account to replace V with Nb. In vitro studies have showed that the cells behave differently

Element	Ti6Al4V Wrought	Ti5Al2.5V Wrought	Ti6Al7Nb Wrought
Aluminium	5.5-6.75	4.5-5.5	5.5-6.5
Vanadium	3.5-4.5	-	Max.0.5 tantalum
Iron	Max.0.3	2-3	Max.0.25
Niobium	-	-	6.5-7.5
Oxygen	Max.0.2	Max.0.2	Max.0.2
Carbon	Max.0.08	Max.0.08	Max.0.8
Nitrogen	Max.0.05	Max.0.05	Max.0.05
Hydrogen	Max.0.015	Max.0.015	Max.0.009
Titanium	balance	balance	balance

Table 1. Chemical composition of titanium based alloys as implants for surgery [49]

in the presence of clutches generated by the wear of the two alloys. There is an increased release of prostaglandin E2 in response to contact with Ti-6Al-4V particles, and an increase in the release of other inflammatory cytokines compared to Ti-Al-Nb particles. These data suggest that Ti-6Al-4V stimulates phagocytic cells more than the Ti-Al-Nb and pure Ti. Exposure of bone marrow cells to Ti-6Al-4V particles induce a significant increase and release of proinflammatory and osteolytic mediators which are responsible for loss of dentures. Stainless steel alloys were widely used in the past because they were cheap, easy to process and with very good mechanical properties. However, stainless steel is very susceptible to corrosion in salty environments, as the tissue fluid is. By corrosion steel becomes a metal with low resistance to fatigue, the main cause of implants failure. The released corrosion products also determined inflammatory side-effects [14, 31]. In the endosseous implants, the inflammation prevents osseointegration and favours fibrous capsule formation. Stainless steels are steels that contain more than 12% Cr. Chromium plays a protective role in steels, this metal having a high tendency to passivation. In this case too, passivation tendency occurs discontinuously, i.d., at 1/8, 2/8, 3/8 chromium percents. The spectacular growth of the potential for positive values occurs in 12.5% chromium atoms as shown in Figure 2.4.a. The percentage of chromium required to achieve stability depends on the immediate work environment. Thus, in a solution of 33% HNO₃ 7% Cr solution is enough, and for FeSO₄ solution 20% Cr is required. The first type of stainless steel used for implants was vanadium steel (18-8V), but its resistance to corrosion was not so good. To increase its resistance to corrosion, molybdenum was added (18-8Mo), which later became 316 stainless steel. In the 1950s, the carbon content of the 316 stainless steel was reduced from 0.08% to 0.03% in order to increase resistance to corrosion. Today it is known as the *316L stainless steel* and it has the following chemical composition: 0.03% carbon, 2% magnesium, 17-20% chromium, 12-14% nickel, 2-4% molybdenum and other elements in smaller quantities such as phosphorus, sulphur and silicon. The passive layer (resistant to corrosion) of these alloys is not as strong as in the case of titanium alloys. For this

reason, stainless steels are used only for temporary medical implants such as screws and orthopaedic rods for fixation of fractures. In dentistry it is used for bolts, for dental coverage, to produce the nets in the dentures.

The problems raised by these steels in use as biocompatible materials are related to the loss of Ni ions, in particular as a result of the corrosion process. These ions are tolerated by the body only in small amounts.

Another large group of alloys used in prosthetic reconstruction is the Co-Cr alloys or stellites. They are cobalt based alloys with chromium as the main element and the alloying elements: molybdenum, nickel, titanium, tungsten added to improve the properties. These elements have a complex action, some of them dissolving producing solid solution hardening, but most form intermediary compounds that increase resistance to corrosion and mechanical properties. Chromium increases resistance to corrosion and oxidation forming an oxide film (Cr_2O_3) on the surface, thus ensuring continuous adherence and protection. On the other hand, chromium forms complex carbides with a role in increasing the mechanical properties. Nickel forms with cobalt a series of solid solution. It has an influence on mechanical properties and resistance to corrosion. Molybdenum lowers the allotropic processing temperature and improves mechanical properties by the densification of the solid solution, due to the formation of c compounds of MoCo_3 , MoCo_7 . Molybdenum contributes to a fine structure, resulting from the process of casting and forging. Tungsten increases the resistance to oxidation and density due to the formation of compounds of WCo_3 and carbides, if the alloy contains carbon. Four standard types of alloys are standardized (after ASTM): F62- Co-Cr-Ni-Mo (forged), F63- Co-Ni-Cr-Mo (forged), F76 - Co-Cr-Mo (cast), F90- Co-Cr-W-Ni (forged). Higher fatigue resistance and breaking of the CoNiCrMo alloy make it highly suitable for applications requiring long life, without cracking or material fatigue. Regarding the resistance to corrosion of Co alloys, they show characteristics similar to the stainless steels, having the advantage of practically zero toxicity.

Alloy	Metal converted into compound, $\text{ng}/\text{m}^2\text{h}$	Metal found in tissue, $\text{ng}/\text{m}^2\text{h}$
Stainless steel – mechanically polished	7, 8	0.274
(AISI 316L) – chemically polished	230	-
Vitallium – mechanically polished	150	0.249
(CoCrW-Ni alloy) – chemically polished	20	-
Ti – mechanically polished	4, 1	0.430
– chemically polished	3, 5	-

Table 2. Corrosion rates of biomaterials in Hank's solution [49]

In conclusion, choosing a metal should be based on the corrosive properties. Metals used nowadays as biomaterials include gold, Co-Cr alloys, 316 stainless steel, titanium, Ni-Ti alloy

and Ag-Hg amalgam. Noble metals are resistant to corrosion and they would be the ideal materials if resistance to corrosion were the only condition. Gold is often used in dental reconstruction offering high performance and longevity. Titanium is a metal which forms a strong passivating layer, remaining passive under physiological conditions. Corrosion currents in normal saline conditions are very weak: 10^{-8} A/cm². Titanium implants apparently remain unchanged. Ti provides superior resistance to corrosion, but it not as hard and resistant as steel. Co-Cr alloys, as the Ti too, are passive in the human body. Stainless steels contain sufficient chromium to have resistance to corrosion by passivation. The passive layer is not as strong as in the case of Ti or Co-Cr alloy. The most resistant to corrosion among the stainless steels are austenitic steels and are symbolized: 316, 316L, 317 (AISI) and 10TiMoNiCr175, 2MoNiCr175 (STAS) containing Mo.

Dental amalgam is an alloy of Hg, Ag, and Sn. Although the stages are passive to neutral pH, the transpassive potential for the γ_2 phase is exaggerated due to the interphase galvanic couples or their cells due to different aeration in the denture. Therefore, the amalgam corrodes and it is often the most active corrosive material used in dentistry.

2. Assessment of metal and dental alloys corrosion

Depending on the state of the environment in which it occurs and of its appearance, corrosion can be: dry corrosion caused by contact of the metal with the oxygen in the atmosphere and humid or galvanic corrosion, which occurs if the metal is in a humid environment, by the occurrence of electrolytic cells. Corrosion is uniform if it occurs on the whole surface of the metal or localized corrosion if it occurs only in specific points on the surface of the metal, being more dangerous.

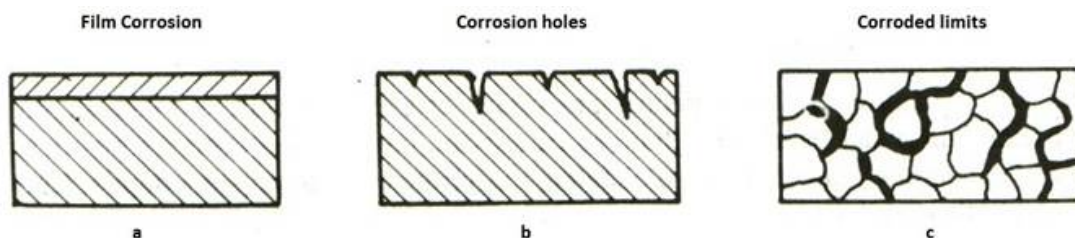


Figure 1. Types of corrosion: a– uniform; b– punctual; c– i ntercrystalline (at the crystal grains limit) [50, p.68]

The types of corrosion indicated are electrochemical corrosion, based on the formation of local galvanic elements at the contact of two metals with different electrode potential in the presence of an electrolyte. Electrochemical corrosion is the destruction of metals or alloys process in the presence of electrolyte solutions, by the electrochemical reactions that involve a transfer of ions and electrons under the influence of a difference of electric potential [10, 11, 37]. Metals release electrons by oxidation and its positive ions go into the solution. Formation of ions and electrons creates an electrical potential E (expressed in volts) to the material-solution interface called

electrode potential which value depends on the nature of the metal on the one hand and on the other hand on the type of the solution. The electrode potential cannot be measured as such, but only the difference of potential at the terminals of a cell formed by a complete electrochemical chain. If the electrode inserted to form the chain is well-defined and stable, it is considered as a reference, making thus possible to compare different electrodes between them in relation to the reference adopted. The reference electrode is the hydrogen electrode, for which the oxidation process is described by the equation: $H_2 \rightarrow 2H^+ + 2e^-$.

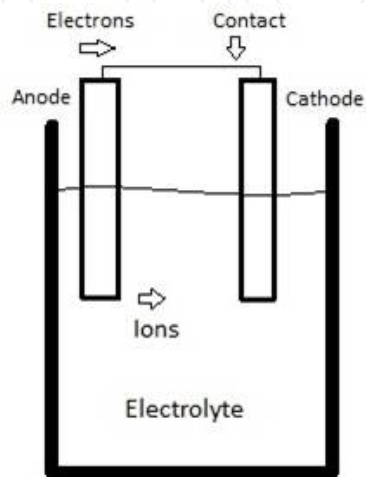


Figure 2. Electrochemical cell [49]

The electrolyte containing ions in solution which are also present in body fluids closes the electrical circuit. Chemical reactions that occur at each of the two electrodes of a galvanic cell (fig. 2) are called electrode reactions. Corrosion is a mixed process developing as follows:

- the anodic ionization reaction of metal and dissolution in the electrolyte of positively formed ions: $M \rightarrow M^{z+} + ze^-$, or $M + zH_2O \rightarrow M(OH)_2 + zH^+ + ze^-$
- takeover cathode reaction of electrons remained in the metal phase, by an existing electron acceptor existing in the solution; the agent is able to reduce itself has nobler potential equilibrium than the of the metal and is called depolarizing ($D + ze^- \rightarrow Dze^-$).

The tendency of metals to enter into the corrosion process is most simply expressed by standard electrochemical series of Nernst potentials (the table [47]). These potentials are obtained by electrochemical measurement in which an electrode is a standard hydrogen formed by a hydrogen bubble over a layer of platinum fine powder. The potential of this reference electrode is considered to be zero. Noble metals are those with a potential higher than the standard hydrogen electrode and base metals have lesser potential.

If two similar metals are present in the same environment, the one which is the most negative in the galvanic series becomes an anode and it shall corrode. The process is called bimetallic or galvanic corrosion and it can be much faster than the corrosion of a single metal.

Element	Electrode reaction	Electrode potential [V]
Lithium	$Li \rightarrow Li^+ + e^-$	- 2.959
Rubidium	$Rb \rightarrow Rb^+ + e^-$	- 2.925
Potassium	$K \rightarrow K^+ + e^-$	- 2.294
Calcium	$Ca \rightarrow Ca^{2+} + 2e^-$	- 2.763
Sodium	$Na \rightarrow Na^+ + e^-$	- 2.714
Magnesium	$Mg \rightarrow Mg^{2+} + 2e^-$	- 2.37
Beryllium	$Be \rightarrow Be^{2+} + 2e^-$	- 1.85
Aluminium	$Al \rightarrow Al^{3+} + 3e^-$	- 1.69
Titanium	$Ti \rightarrow Ti^{2+} + 2e^-$	- 1.63
Zinc	$Zn \rightarrow Zn^{2+} + 2e^-$	- 0.761
Chromium	$Cr \rightarrow Cr^{2+} + 2e^-$	- 0.71
Chromium	$Cr \rightarrow Cr^{3+} + 3e^-$	- 0.50
Iron	$Fe \rightarrow Fe^{2+} + 2e^-$	- 0.44
Cadmium	$Cd \rightarrow Cd^{2+} + 2e^-$	- 0.42
Nickel	$Ni \rightarrow Ni^{2+} + 2e^-$	- 0.23
Tin	$Sn \rightarrow Sn^{2+} + 2e^-$	- 0.14
Tin	$Pb \rightarrow Pb^{2+} + 2e^-$	- 0.13
Iron	$Fe \rightarrow Fe^{3+} + 3e^-$	- 0.045
Hydrogen	$H_2(g) \rightarrow 1/2 (H^+ + e^-)$	0.000(reference)
Copper	$Cu \rightarrow Cu^{2+} + 2e^-$	+0.337
Oxygen	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	+0.401
Copper	$Cu \rightarrow Cu^+ + e^-$	+0.522
Silver	$Ag \rightarrow Ag^+ + e^-$	+0.797
Mercury	$Hg \rightarrow Hg^{2+} + 2e^-$	+0.798
Platinum	$Pt \rightarrow Pt^{2+} + 2e^-$	+1.20
Oxygen	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	+1.229
Gold	$Au \rightarrow Au^{3+} + 3e^-$	+1.50

Table 3. Electrochemical series (normal electrode potential of hydrogen reduction) [47, p.92]

The potential difference E given by the concentration of metal ions in solution according to Nernst equation, is given by: $E = E_0 + (RT / nF) \ln [M^{n+}]$, where E_0 is the standard electrochemical potential, T is the absolute temperature, F is Faraday constant, (coulombs / mols), and n is the number of ions. The precedence of nobility observed in practice can be different as the one thermodynamically prescribed. Due to the phenomenon of passivation (metals cover with a passivation layer of reaction products, which protects the metal from further attack).

Localized corrosion can be, in its turn, crevicular or galvanic corrosion. Often, in the case of dry uniform corrosion, following the process of corrosion, a layer of corrosion products is formed on the surface of the metal, which are nothing else than the metal oxides. By thickening of the oxide layer, the metal surface shall be protected from exposure to the atmospheric oxygen and thus the corrosion process shall be self-limited in time. This type of corrosion

occurs in metals where oxides formed are very stable. There are also oxides that are not as stable, so that the oxide layer can crack or run-out from the surface of metal and then the corrosion continues over time.

In the oral cavity, corrosion of metals and alloys is produced electrolytically in humid environment, so it is a galvanic corrosion. Galvanic corrosion occurs when an electrolytic cell is formed. For an electrolyte cell to form, an electrolyte (a liquid which can lead electricity, in our case saliva), an anode (electrode providing/giving up electrons) and a cathode (electrode receiving electrons) are needed. If two metals with different electrical potentials are found in wet environment, metal with a more negative electric potential (see table) shall oxidize, so it shall lose electrons becoming an anode, and the metal with a more positive electric potential shall become the cathode. There are significant differences between the oxidation potential of the various metals. The more susceptible to oxidation, the more reactive they are, with higher corrosion potential. The potential for corrosion of metals depends on their reactivity, i.e. their galvanic potentials. Galvanic corrosion can occur between two different metals or alloys, but galvanic corrosion is more insidious and difficult to detect occurring in the same alloy that is composed of different phases, with different oxidation rates.

Crevicular corrosion occurs if there is a crack in the metal surface, which can be filled with liquid saliva, meaning there are anaerobic conditions. However, the metal shall release the ions resulting from the corrosion process, but these released electrons shall not be able to react in the crack depth where there is no oxygen. Therefore they shall be forced to migrate to the surface of the crack, where the oxygen shall produce the oxidation reaction. This flow of electrons from the base to the surface of the crack, the crack base shall become the anode and the surface shall become the cathode, actually leading to the formation of an electrolytic cell, with loss of substance in the crack depth. As more corrosion products are formed, they tend to be deposited in the crack, further reducing the supply of oxygen at the base of the crack, thus increasing the potential difference between the core and the surface. Thus, the process is self-sustaining. This type of corrosion is more dangerous than others because by this mechanism, any microfissures in the metal surface is transformed over time, slowly, into deep fractures that shall lead to breaking the metal below its strength and often without any warning that this may happen.

In conclusion, the effects of corrosion on the dentures and organism in general are varied and consist mainly in the loss of metal ions, forming galvanic microcurrents (oral galvanism), metallic taste (due to the release of metal ions), opacity, adverse biological effects (rare).

If metal restorations are present in the oral cavity at a time from metals with very different electrical potentials in combination with oral fluid (which acts as the electrolyte), as we have seen, an electrolysis cell appears. The phenomenon is more intense if the two different metals are in contact, e.g. adjacent teeth. Under such circumstances, due to the difference of potential microcurrent galvanic occur, which results in pain in the pulp and/or metallic taste. This phenomenon is known as oral galvanism. With the occurrence of specific symptoms or signs of oral galvanism, it is necessary to replace one the metallic constructions with a non-metallic reconstruction.

Experimental studies have shown that in oral galvanism electrical currents occur with relatively high tensions. The threshold varies from patient to patient, most of them being sensitive to values between 20 and 50 μA . Oral Galvanism manifestations can be varied, with symptoms such as metallic taste, burning sensation, pain in teeth with metallic reconstruction (due to galvanic microcurrents), and trigeminal neuralgia. Objectively they are manifested by gingivitis and glossitis, hypertrophy and turgor of the lingual papilla, erosion and ulceration of the oral mucosa, late leukoplakia (4-5 years after application of dentures).

Galvanic corrosion in the oral cavity can be prevented by using the same type of alloy for all metal prosthetic reconstructions in the mouth, especially for those that come in direct contact. At the same time, the use of homogeneous alloys, which cannot produce potentially different phases, reduces the risk of intrinsic galvanic corrosion of the alloy or perfect polishing of metal works (dentures or amalgam obturation) which reduce the risk of crevicular corrosion.

From the thermodynamic point of view [9, 46, 47] the tendency of metals to pass in the ionic state differ greatly from one metal to another and it can be energetically characterized by the variation in enthalpy (ΔG), which accompanies the process. Electrochemically, the enthalpy variation equals the electrical work performed by an equivalent of gram ions: $\Delta G = -Z F E$, where: E – electromotive tension of the cell in which the anode and cathode reversible reaction of the corrosion process is achieved; Z – number of electric charges involved in the reaction; $F=96500$ coulombs / equivalent gram; $E = E_C - E_A$, where: E_C - equilibrium potential of the cathode; and E_A - equilibrium potential of the anode. As it is well known a reaction of thermodynamically possible if it is accompanied by the decrease of the free enthalpy, namely $\Delta G < 0$. Correlating the relationships above it is obtained: $E_C < E_A$, stating that, the electro-chemical corrosion of a metal can occur if the equilibrium potential of the metal in the given solution is more electronegative than the equilibrium potential of a depolarizing in the solution.

Chemical stability of the metal and the type of the different corrosion products depend on the electrode potential and the pH^* of the solution. Graphically, the equilibrium between metal and its various oxidizing species is represented by the diagram “potential – pH ” in isothermal conditions or thermodynamic stability diagram called Pourbaix diagram. This provides thermodynamic data on the phenomenon of corrosion, indicating the equilibrium conditions of all reactions that can take place between the metal and the aggressive environment at a given temperature. Pourbaix diagram includes: the immune area where corrosion is energetically impossible, the conditions of corrosion area where the metal ionization occurs (corrosion), the passivity conditions area where the ionization of the metal is thermodynamically possible, but it does not occur due to the formation of a passivating film on the metal surface; in the passivation area, the stable solid constituent is an oxide, a hydroxide, a hydrate or a salt of the metal. In the case of biomaterials the significance of the Pourbaix diagram can be described as follows: different parts of the body have different pH and different oxygen concentrations. For example, a metal which behaves well (it is immune or passive) in a particular part of the body can have an enhanced corrosion elsewhere. Moreover, the pH may change its value in tissues that can be injured or infected. An ordinary liquid in the tissue has a pH of about 7.4, but in a wound it may drop to 3.5, and in infection can increase to 9.0 [24],

(*)-by definition $pH = -\log [H^+]$, where $[H^+]$ is the concentration of H^+ ions. The product $[H^+][OH^-]$ equals to 10^{-14} . For neutral solutions $[OH^-] = [H^+]$ and $pH=7$. A $pH < 7$ indicates an acidic solution (excess of H^+ ions) and a $pH > 7$, an alkaline solution (OH^- ions excess).

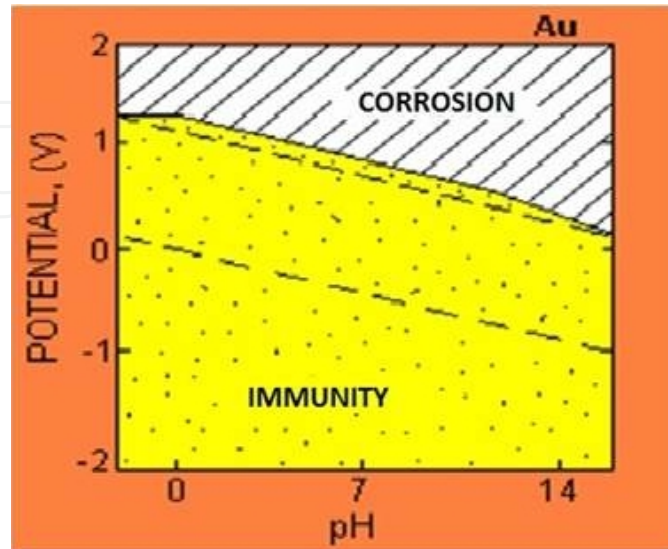


Figure 3. Pourbaix diagram for an immune metal (gold) (after M.Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions, NACE, Houston/CEBELCOR, Brussels, 1974) [47, pag.56]

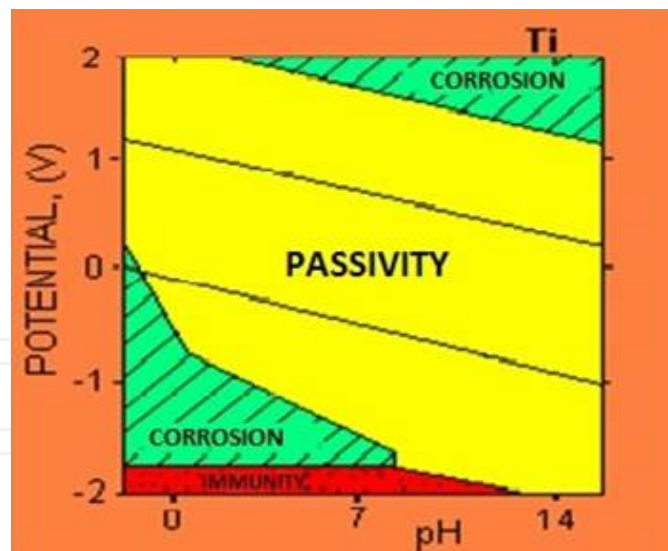


Figure 4. Pourbaix diagram for a passive metal (titanium) (after M.Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions, NACE, Houston/CEBELCOR, Brussels, 1974) [47, pag.56]

Pourbaix diagrams are useful, but are limited as they allow determining only the thermodynamics possibility of occurrence of a corrosion reaction. Completing them with kinetic data provides a real and useful guidance to assess/evaluate the level of metal's destruction in the specific environment.

Kinetics of electrochemical corrosion means the assessment of the *corrosion rate* which sets the rate of corrosion of a metal under the influence of the corrosive agent. The corrosion rate can be determined by direct methods and indirect methods. Direct methods determine the gravimetric index, or the index of penetration.

The *gravimetric index* or the *corrosion rate* (V_{cor}) is the change in sample mass (Δm), as a result of corrosion, per surface area unit (S) per time unit (t): $V_{cor} = \Delta m / (S t)$ which is usually considered as $g/m^2 h$. It is the most common way of expressing corrosion, being able to express the gain of weight of the sample, forming the corrosion products (metal oxidation) that remain adherent to metal or weight loss when corrosion products can be removed from the surface. The gravimetric index introduces errors in determination, as exact chemical composition of the corrosion products is not known. Therefore, the most used index is that corresponding to the weight loss, its precision depends on the removal of all corrosion products.

The *penetration Index* (I_p) is the depth by which the corrosion penetrated in the mass of metal, for one year. It is calculated from the gravimetric index V_{cor} and metal density ρ [g/cm^3] as follows: $I_p = (24 \cdot 365 \cdot V_{cor}) / (1000 \cdot \rho)$ where 24 is the number of hours in a day; 365 – the number of days in a year; 1000 – the conversion factor of the measurement units.

Indirect methods to assess the rate of corrosion consist of electrochemical, electrical, acoustic, optical, etc. measurements. The electrochemical methods assess the quantity of corroded metal by measuring the current flowing in this process. If for each metal equivalent gram passed in solution, 96 500 coulombs are released, then for the electricity quantity the amount of electricity “ It ” flowing during corrosion, the amount of corroded metal “ m ” shall correspond. According to Faraday Law we can write: $m = Kit = \frac{A}{ZF} It$

The *corrosion speed* can be obtained comparing this quantity to the surface S and time t :

$$V = \frac{m}{St} = \frac{A}{ZF} \cdot \frac{It}{St}; \quad V = \frac{A}{ZF} \cdot \frac{I}{S} = K.$$

Current density I , in A/cm^2 ,

$$I = \frac{K Z F}{10^5 \cdot A}, \text{ where: } K - \text{ is the average corrosion speed; } Z - \text{ valence of the ion that passes into the solution; } F - 26.8 \text{ A/h.}$$

Potentiodynamic methods provide useful information on the susceptibility of metals and alloys to generalized or pitting corrosion.

The evolution of the electrode potential in the open circuit is used as a corrosion behaviour criterion. This potential can vary over time as changes occur at the electrode surface (oxidation, formation of the passive layer or immunity). The physical and chemical reactions on the surface of the material change the solid-solution interface, which explains the development of the potential. After a period of immersion, it stabilizes around a stationary value.

Pitting corrosion and crevice corrosion is emphasized by cyclic polarization curves (CV/cyclic voltammetry). Cyclic polarization tests are commonly used to assess the susceptibility of

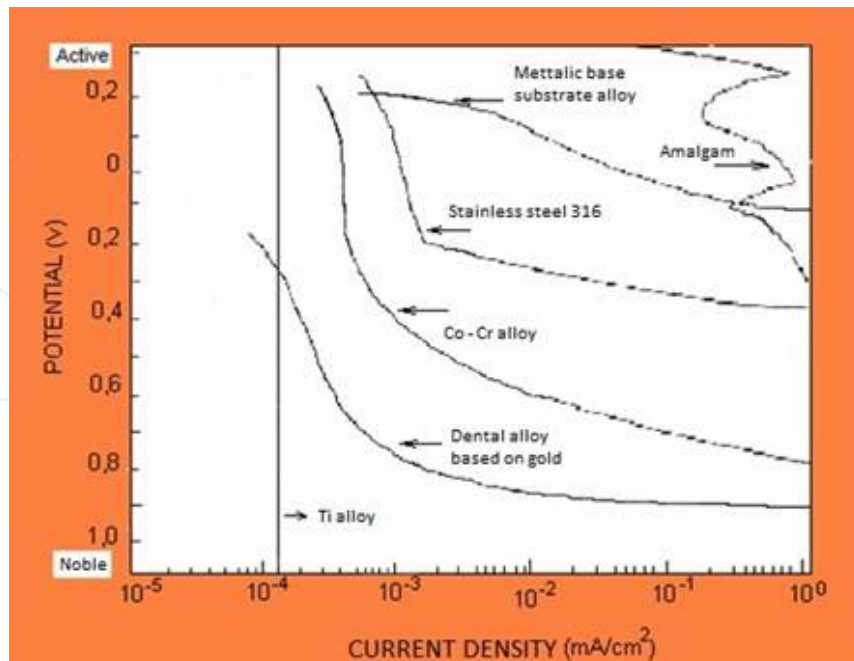


Figure 5. Curves of potential - current density for some biomaterials. (E.H.Greener, J.K. Harcourt, E.P. Lautenschlager, Materials Science in Dentistry, Williams and Wilkins, Baltimore, 1972) [47, pag.58]

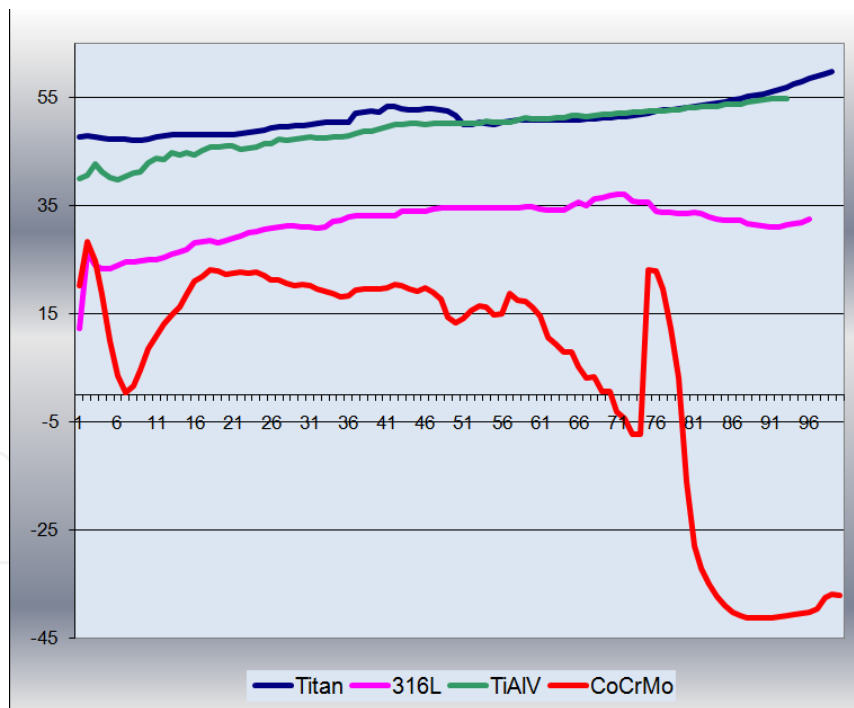


Figure 6. General diagram on the results of assessment tests of stationary potential variation [51]

metals and alloys to pitting corrosion (the hysteresis curve indicates pitting corrosion). The electrochemical impedance spectroscopy provides important information about the tendency of the alloy to the generalized corrosion process.

Conclusions

Pure titanium:

- the anodic curve has an active area between -0.19mA/cm^2 at a potential of -0.61V .
- Voltammetric curves show that the hysteresis area is small and negligible, which means that the Biomet not present and is not sensitive to the types of localized corrosion.

Alloyed Ti (Ti6Al4V):

- both the alloyed titanium and pure titanium indicate that the active corrosion area is very small or almost absent for pure titanium;
- experimental parameters: current density displays values from -0.15 to 0mA/cm^2 ; potential range is between 0.96 and 0.57V ; the return voltammetry curve shows a small hysteresis compared to the previous biomaterial samples analyzed.
- the assessment of the voltametric cycle of the titanium alloy indicates that this biomaterial has a very good resistance to localized corrosion and general corrosion. These low values of corrosion are considered by the values of the maximum corrosion current, of the passivation current and the field of potential, when the current density is constant.

Voltammetric cycles (see figure6) - Comparative analysis indicates that in case of titanium and titanium alloy there is a surface unaffected by corrosion, result which is in correlation with diagrams obtained after the electrochemical tests. In case of 316L stainless a clouding of the submerged surface can be noticed and the occurrence of corrosion points.

3. Corrosive degradation-resin based composites

The introduction of resin-based composite dental materials around 1960s was a revolution in restorative dentistry. Resin-based composites are possibly the most used materials available in modern dentistry as they are used in a large variety of clinical applications, ranging from filling materials, luting agents, indirect restorations and metal facings to endodontic posts and cores. Composite restorative materials represent one of the many successes of modern biomaterials research, since they replace biological tissue in both esthetics and function. In anterior teeth composite is the clear material of choice among general dental practitioners. Direct composite restorations are increasingly employed also to restore posterior teeth due to their low cost and less need for the removal of sound tooth substance when compared to indirect restorations, as well as to their acceptable clinical performance [60].

Composite restorations must withstand an aggressive environment that is different from patient to patient. Mastication forces, occlusal habits, abrasive foods, chemically active foods and liquids, temperature fluctuations, humidity variation, bacterial by products, and salivary enzymes all contribute uncontrollable factors that affect composite restoration longevity [61].

To estimate how long posterior composite restorations last, the long-term studies are the ones to identify modes of failure and possible reasons for these failures. In the most recent review

made by Demarco et al. 2012 [61] it has been searched the dental literature looking for clinical trials investigating posterior composite restorations over periods of at least 5 years of follow-up published between 1996 and 2011. As observed in their literature reviewed, a long survival rate for posterior composite restorations can be expected provided that patient, operator and materials factors are taken into account when the restorations are performed. The majority of the clinical studies indicated that annual failure rates between 1% and 3% can be achieved with Class I and II posterior composite restorations depending on several factors such as tooth type and location, operator, and socioeconomic, demographic, and behavioral elements. The material properties showed a minor effect on longevity. The results of this review reconfirmed that the main reasons for failure in the long term of composite restorations were secondary caries, related to the individual caries risk, and fracture, related to the presence of a lining or the strength of the material used as well as patient factors such as bruxism.

Taking into account the caries risk impact on the longevity of resin based composites materials is suggested that future composite research be directed toward developing materials that will suppress bacterial activity at the tooth-composite interface and counter the effects of caries [67,68,69,72]. Concern still exists when the composite materials are placed in high stress situations, especially in patients with bruxing or parafunctional habits or when placed in large preparations, perhaps on several teeth in a quadrant, and when used to replace cusps. The concern here is for fracture of the restoration as well as wear [60].

Degradation in dental composites may result in matrix and/or filler deterioration, due to mechanical and/or environmental loads, interfacial debonding, microcracking, and/or filler particle fracture. A continuous application of mechanical and environmental loads eventually leads to progressive degradation and crack initiation and growth, resulting in catastrophic failure of dental restorations [60-62].

The polymers used in resin composites are susceptible to absorption of solvents, especially water, and the loss of soluble components. The solvent molecule forces the polymer chains apart, causing swelling. As the strength of the bond decreases, the polymer becomes softer, the glass transition temperature is reduced and the strength may be lowered. Water sorption is a contributory factor to discoloration of the restorations and the hydrolytic degradation of the resin-filler interface. The second basic degradation process of the polymeric matrix involves the scission or breakdown of the covalent bonds. The scission of the polymer chain will reduce the molecular weight of the polymer, thus resulting on a significant loss of mechanical properties.

J.L.Drummond [62] has made a valuable review of the mechanisms and degradation effects due to aging of the resin based composites. During exposure to various environments, dental composites are subjected to material property changes due to degradation and aging. He concluded that these changes are due to: (a) chemical breakdown by hydrolysis; (b) chemical breakdown by stress-induced effects associated with swelling and applied stress; (c) chemical composition changes by leaching; (d) precipitation and swelling phenomena to produce voids and cracks, leaching the interface; and (e) loss of strength due to corrosion.

All of these degradation processes may lead to nucleation and the growth of microcracks. Over time, the leaching of the soluble components, the swelling and degradation of the cross-linked polymer matrix in the dental composite, and hydrolysis of the filler-matrix silane interfaces

eventually lead to a decrease in mechanical properties. With respect to fracture toughness, water seems to lower the yield stress, release internal stress accumulated during polymerization shrinkage, and increase the plastic zone ahead of the crack, which causes the increase in observed fracture toughness. Other theories as to the cause of the degradation of the dental resin include the formation of microcracks through repeated sorption/desorption cycles, leading to hydrolytic degradation of the polymer [62]. The extent of water uptake is dependent upon the monomer formulation and promising lower water uptake are observed for silorane-based systems already used by the practitioners as a filling alternative to the dimethacrylate-based composites. But as newer formulations of composites are designed to be self-adhesive, they will most likely be even more hydrophilic than current resins [59, 60].

Biotribocorrosion is a material degradation process due to the combined effect of corrosion and wear. Too little attention was given to the corrosive degradation of resin based composites in the dental literature so far. Most of research has focused on the clinical implication of the corrosive wear in the overall wear phenomenon of teeth and restorative materials [64-66]. Wear of teeth and restorative materials is the result of different complex processes that depend primarily on the abrasive nature of food, the properties of the antagonistic material, the thickness and hardness of enamel, the chewing behaviour along with parafunctional habits, and neuromuscular forces. Different wear phenomena may take place in the oral cavity. An overview of the types of wear, grouped as biotribocorrosion has been made by Lambrechts et al 2006 [64]. Wear as function of a tribological system is composed of three basic elements [64]: (a) the structure—the types of materials in contact and the contact geometry; (b) the interaction conditions—the loads, stresses, and duration of interaction; and (c) the environment and surface conditions—including the surface environment and chemistry, surface topography, and ambient temperature.

Wear tribology and biotribocorrosion define wear as a complex phenomenon and an 'overall effect' of a number of interrelated processes. Depending on the parameters of the tribosystem the wear processes could be described with five terms [64]: two-body abrasion, three-body abrasion, fatigue wear, tribochemical wear (dental erosion, corrosion wear), adhesive wear. Abrasive wear describes the ploughing of hard asperities into softer surfaces, and may be further distinguished between abrasion and attrition. Abrasion occurs during mastication processes in the presence of food serving as a third body (three-body abrasion, whereas attrition is the result of direct contact of antagonistic teeth or restorations during mastication, swallowing, or occlusal movements as a two-body abrasion. Fatigue wear and corrosive wear are considered two important types of biotribocorrosion. Fatigue wear describes a process that is caused by subsurface cracks that proceed due to repeated load cycles, and tribochemical wear relates to a chemical reaction producing a surface layer that can be scraped away by antagonistic contact [62, 63].

Tribochemical wear [65] or corrosive wear [70] is caused when chemicals weaken the intermolecular bonds of the surface and therefore potentiate the other wear processes. There is an interplay of erosion, attrition and three body abrasion in tooth wear. In the mouth this effect is normally caused by acids, which may be 'extrinsic' such as dietary acids or 'intrinsic' resulting from gastric reflux. On exposure to plaque acids, food-simulating constituents, and enzymes, resin composites have undergone softening and roughening [71, 78]. The most important thing to understand is that acids weaken only the surface molecules. In general, the

corrosion is rapid initially, and tends to slow down, or it may even cease completely, after a cohesive film has been formed on the surface. However, when this pellicle is removed by the sliding of surfaces that meet over it, an unaltered surface is exposed, and the chemical attack continues. Mechanical tooth wear and chemical dissolution act simultaneously. Consequently, resin composites may show an increased abrasive wear rate.

Improvements in the properties of dental resin composites are constantly being sought. Given that secondary caries and fracture are the two primary reasons given for replacement of dental composites, it is warranted to continue to pursue improvements in wear resistance, as well as shrinkage and its accompanying stress. Shrinkage stress is often considered the most significant problem with current restoratives and a primary contributor to premature failure in composite restorations, since it is capable of deforming tooth structures and causing microcracks and adhesive failure [67]. This process is further assisted by voids introduced during material processing, imperfect interfaces, and residual stresses, making resistance to crack initiation and growth an important consideration for a reliable assessment of dental restorations. The gaps between dentin and adhesive system couldn't be attributed also to the shrinkage stress that accompanies the polymerisation process, but to the lower efficiency of the self-etch mechanism of adhesion [67] (Figure 7, 8). The marginal crevice caused between restoration and tooth by the polymerization shrinkage of the composite together with the voids between the adhesive layer and enamel/dentine where oxygen deficit can form can be considered sites prone to oxygen concentration cell attack or crevice corrosion and further studies are needed to demonstrate this.

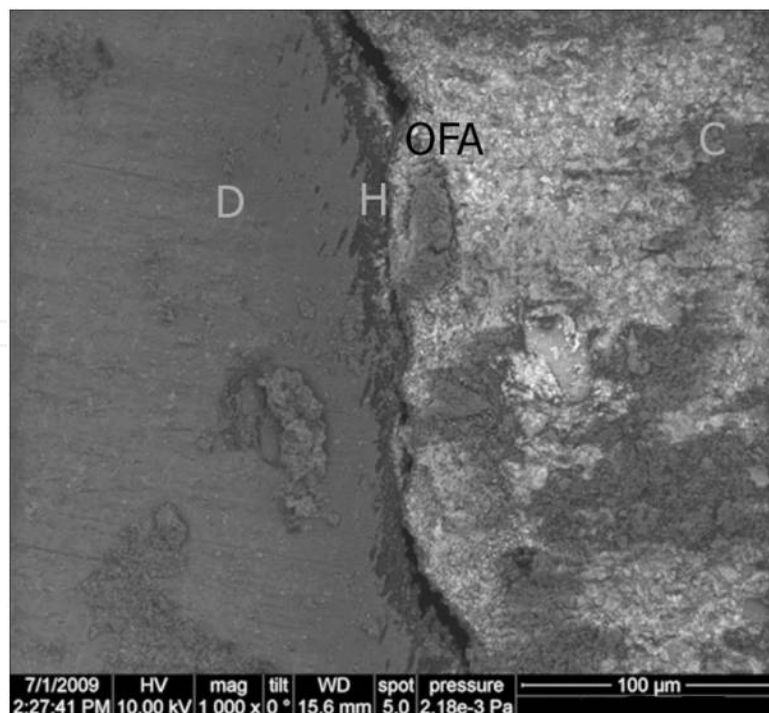


Figure 7. FE-SEM images of a sectioned restorations 1000X. Restoration/dentin interface of the cavity floor of dymethacrilate resin based composite. D-dentine, C-composite, OFA-adhesive OptiBond FL, H-Hybride layer, G-gap [79, 80]

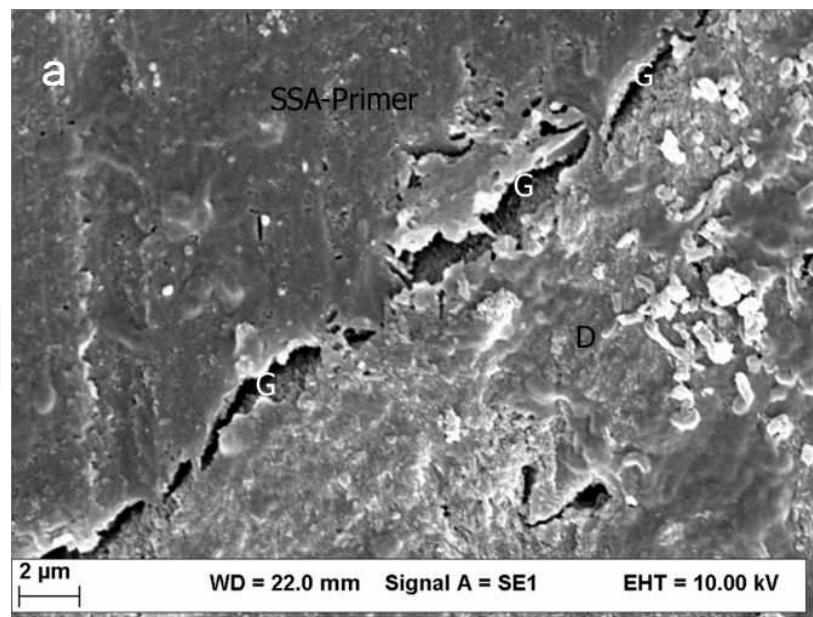


Figure 8. SEM images of sectioned restorations. Restoration/dentin interface of the cavity floor of a silorane based composite Filtek™ Silorane restoration (FS- Filtek™ Silorane, SSA -Primer-Silorane Adhesive System Primer, D- Dentin, G- gap [80].

The longer a restoration is in the clinical service life, the higher the failure rate, but the failure of resin composite restorative materials is far more complicated than just the material properties. As with all dental restorative materials, the proper technique, the appropriate materials, proper patient selection and monitorisation for repair vs. replacement usually ensure a successful clinical restoration.

4. Evaluation of corrosion for dental ceramics

The commonly and easiest method to investigate the corrosion decay of dental ceramics is to evaluate the weight loss of the samples after immersion in CH_3COOH solution 4%. Two different dental ceramics were investigated: alumina based ceramic (crystal structure) and zirconia based ceramic (Y-TZP, yttrium-stabilized tetragonal zirconia polycrystal structure). Both of them were sintered ceramics. The test sample specimens were rectangular shaped ($l = 12 \text{ mm}$) as the blank ceramic shape with thickness $d = 3 \text{ mm}$ [80].

Samples were washed in distilled water and dried in a sterilized unit at $110 \pm 4^\circ\text{C}$ for 2 hours. After determining the mass of the sample with the accuracy of $\pm 10^{-4} \text{ g}$ (analytic scale, Precisa, 320XT), each sample was immersed in a recipient with CH_3COOH solution 4%. The recipients were placed in an usual thermostatic shaker at temperature $t = 37^\circ\text{C}$ for 4 hours. After the time has elapsed, the samples were washed with distilled water and dried in the sterilized unit at $110 \pm 5^\circ\text{C}$, for 2 hours time and weighed. The results obtained are depicted in Table 4

Sample	Loss weight (average value, $\mu\text{g}/\text{cm}^2$)*
Alumina ceramic	14.30 ± 0.60
Zirconia ceramic (Y – TZP)	5.60 ± 0.60

*SD = ± 0.60

Table 4. Loss weight (average value, $\mu\text{g}/\text{cm}^2$) [80]

An important evaluation of the corrosion process is samples surface investigation by scanning electron microscopy (SEM). Information regarding all stages of corrosion process (galvanic, pitting, crevice and stress) can be obtained. Dental ceramic samples were examined before and after corrosion process according the above mentioned protocol. Results are depicted in Fig.9.

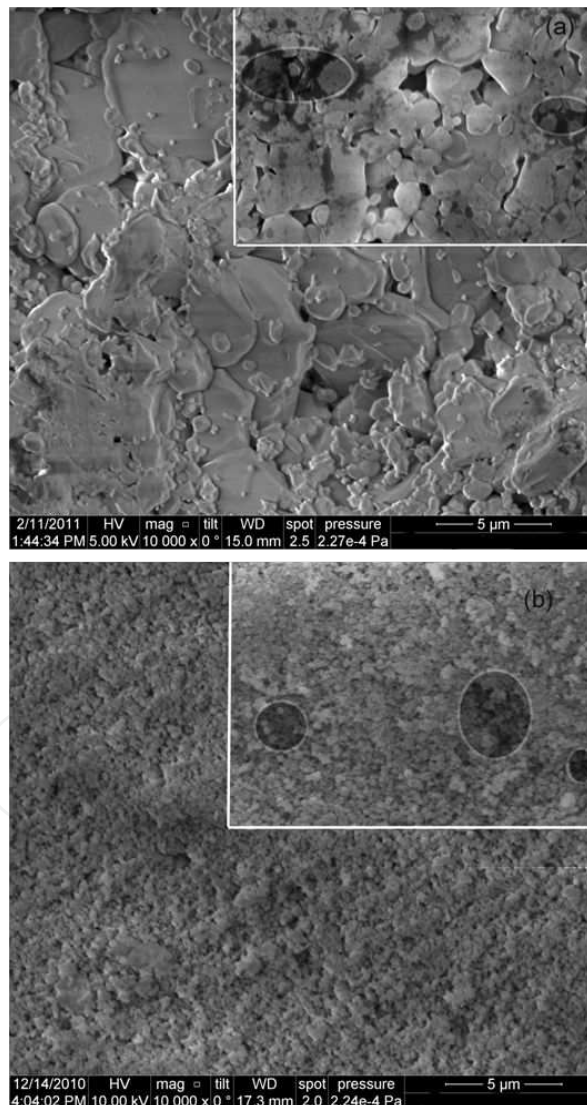


Figure 9. SEM micrographs of dental ceramic samples, before and after corrosion process (insets): (a) alumina ceramic, (b) zirconia ceramic. Details: for insets, shady areas are corresponding to the corroded areas [79, 80, 81]

Examining the sample surfaces quality, we noticed that alumina ceramic sample is more corroded than zirconia sample. It can be observed small holes (gaps) on samples surface, larger for alumina than zirconia sample (Fig. 9). An important detail to be noticed, is that as morphological structure, zirconia is more compact than alumina ceramic [80, 82].

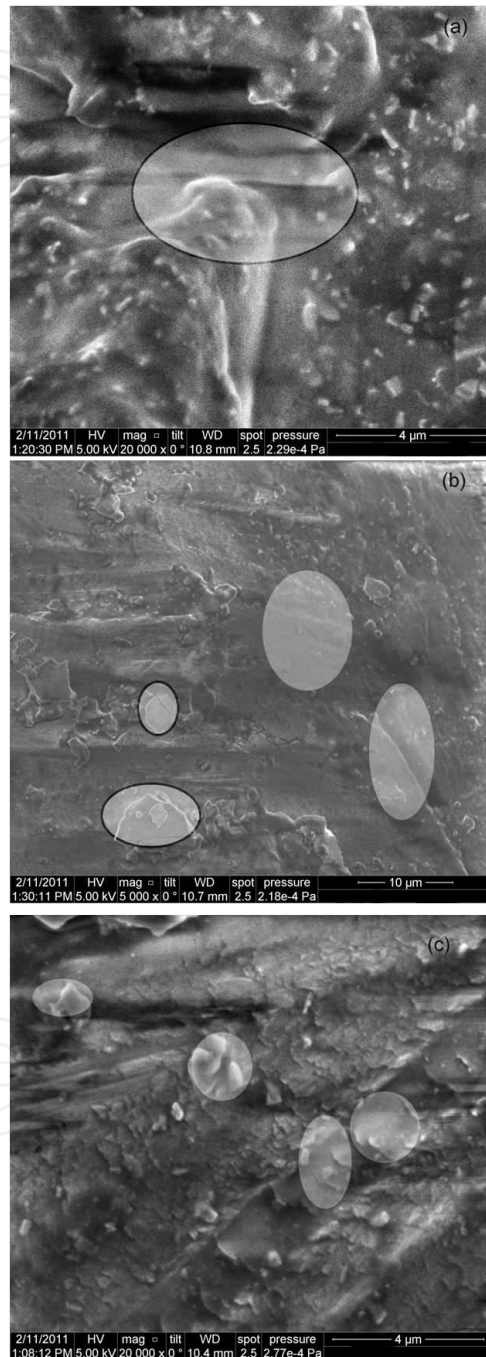


Figure 10. SEM micrographs of a dental restoration work with zirconia core after five years working time. Details: (a) interface zirconia core / dental luting cement, not corroded; (b) interface area affected by crack and crevice corrosion (shady areas) and surface deposits (black border shady areas); (c) surface defects of zirconia dental ceramic core (shady areas) [79, 80]

Relevant for the study is the investigation of a dental restoration work, after a period of working time in the oral biotop. Hence a patient zirconia dental restoration work was investigated, with working time of approximately 5 years. Using SEM technique, there were examined interface zirconia ceramic / dental luting cement and the ceramic core surface (Fig.10).

It can be noticed that the corrosion process (corresponding to the crevice and crack corrosion) is quite aggressive at the interface ceramic / dental luting cement (Fig. 10 (b), available for larger magnification), where small holes along the interface line are observed. Regarding the ceramic core of zirconia work (Fig. 10 (c)), the surface presents defects and areas of stress corrosion and possible failure of the dental work. It is known that zirconia is sensitive to stress corrosion because of changing crystalline phases (T → M, tetragonal to monoclinic phase) [80, 82, 83]. That was the reason the dental work was replaced. Also bacteria deposits on dental ceramic work surface can be observed, those being improved by the surface roughness as is shown Fig. 10 (b), (c). Some areas are presented into good conditions, not affected by corrosion (Fig. 10 (a)) as a sign that a long lasting resistance to corrosion is possible.

Conclusions

- The most efficient way for preventing corrosion effects, is that to minimize (to reduce) those factors conducting to the corrosion process (each type of corrosion).
- Pitting corrosion and crevice corrosion, although similar as mechanism, being initiated by differential aeration phenomena, are different as pitting corrosion is determined by submicroscopic defects, especially manganese sulphides oriented in the direction of deformation (sulphide being plastic), and crevice corrosion is determined by macroscopic defects of the surface oxide layer, these defects may be due to the degree of processing of the surface, respectively the broken pieces on the surface resulting in cells with differential aeration and initiates the crevice corrosion process. The softer the material, the more difficult its processing, and thus the possibility of developing these crevices is greater.
- Galvanic corrosion is the starting point of the corrosion process regarding the oral biotop. Some possibilities may be taken in account for reducing this corrosion effect:
- Reducing as much possible the number of materials used for dental restorations, same materials for the same patient (each material has its own corroding potential);
- As much possible, using materials with similar corroding potential values; corroding potential being a criteria of material biocompatibility;
- Contact or open areas when using metal alloys, as much possible care should be taken to keep them electrically insulated;
- High quality smoothing surfaces (care must be taken during air abrasion process);
- In case of using alumina ceramic, using of zirconia as surface quality improver for given proper conditions of temperature and pressure during dental restoration manufacturing process (before applying veneer and glazer) [82, 83].

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