Galvanic Corrosion Behavior of Dental Alloys

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Additional information is available at the end of the chapter

1. Introduction

There is a wide variety of dental alloys, ranging from nearly pure gold and conventional gold-based alloys to alloys based on silver, palladium, nickel, cobalt, iron, titanium, tin, and other metals (Table 1). The types of dental alloys have increased significantly since 1980s in order to change the market price of gold and palladium. Although gold alloys are the materials of choice in this area because of their high mechanical properties, good corrosion resistance and excellent biocompatibility, their price still poses the essential challenge to dentistry. So that, alternative materials such as Ag-Pd alloys, Co-Cr alloys and Ti alloys have been introduced into dentistry [1,2].

Alloy type	Uses in dentistry	Major elements
Gold-based	Restorations, solders	Au, Ag, Cu, In, Pd, Pt, Zn
Palladium-based	Restorations	Pd, Ag, Ga, Cu
Silver-based	Restorations, solders	Ag, Pd
Cobalt-based	Restorations	Co, Cr, Mo, Fe, C, Si, Mn
Nickel-based	Restorations, orthodontic materials	Ni, Mo, Fe, C, Be, Mn
Titanium-based	Implants	Ti, O, N, C, Fe, H
Iron-based	Implants, orthodontic materials	Fe, C, Ni, Cr
Mercury-based	Amalgam	Hg, Ag, Sn, Pd, Cu, In

Table 1. Common types of alloys in dentistry and their major component elements [1]

Dental alloys can be classified into a variety of applications such as restorations, amalgam, implants, solders and orthodontic materials. The used alloys should have suitable physical, mechanical and chemical properties for mentioned applications. For example, an orthodontic wire is required to have a relatively high flexibility (a low modulus) and the ability to be bent and shaped. However, the alloy for a dental restoration should have almost no flexibility (a high modulus) and be hard and difficult to deform.

Biocompatibility is an important measuring property which should be evaluated first. The word biocompatibility is defined as the ability of a material to perform with an appropriate host response in a specific situation [3]. Although the biological compatibility of dental alloys inclined to be considered separately from the other properties, biocompatibility is rather related to other properties of the alloys such as corrosion resistance which is estimated by measuring the release of the corrosion products themselves. The higher the corrosion rate of the alloy, the greater the metal ion release and the greater the risk of undesirable reactions in the mouth. These reactions may include unpleasant metallic tastes, allergy, irritation or another reaction. Since the release of metal ions depends on electrochemical rules, many efforts have been made to evaluate the biocompatibility of dental alloys via electrochemical analyses [1, 4, 5].

As was mentioned earlier, the corrosion behavior of dental materials is important because poor biocompatibility of the products may render the materials inappropriate for implantation. In general, the word corrosion stands for material or metal deterioration or surface damage in an aggressive environment. The oral environment is also favorable for corrosion in which the metal is attacked by presence of natural agents (air and water), temperature fluctuations (hot and cold meals) and pH changes because of diet (milk products or orange juice), resulting in partial or complete dissolution, deterioration, or weakening of any solid substance [4, 6]

One of the problems associated with the use of metallic materials in dentistry is the probability of galvanic corrosion [2, 4, 7-10]. Generally, galvanic corrosion is either a chemical or an electrochemical corrosion. This phenomenon is attributed to a potential difference between two different metals connected through a circuit for current flow to occur from more active metal (more negative potential) to the more noble metal (more positive potential). In addition, galvanic corrosion is a very complex phenomenon. Six basic factors are involved in galvanic corrosion: (1) potentials, (2) polarization, (3) electrode areas, (4) resistance and galvanic current, (5) the electrolyte medium, (6) aeration, diffusion and agitation of the electrolyte [11]. Galvanic coupling is a galvanic cell in which the more negative metal (anode) is the less corrosion resistant metal than the more positive metal (cathode) [12]. The resulting galvanic couple achieves a mixed potential that reaches between the corrosion potentials of the uncoupled metals (Fig. 1). Due to mutual polarization, the anodic corrosion rate of the anode will be accelerated, while the anodic rate of the cathode will be reduced [10].

In dentistry application, galvanic corrosion occurs when two or more dental prosthetic devices with dissimilar alloys come into contact while subjected to oral liquids like salvia; the difference between the corrosion potentials results in a flow of electric current between them. Therefore, the galvanic cell is formed and causes the increasing corrosion rate of the

anode and enhancing the amount of ion metal released. The galvanic current passes not only through the metal/metal connections, but also through the tissues, which may cause pain. Galvanic currents in the oral environment may cause sharp pain when they exceed 20 mA [13]. Geis-Gerstorfer et al. [14] believes that the galvanic corrosion of dental devices is important in two respects: 1) the biological effects which may result from the dissolution of alloys and 2) the current flow resulting from galvanic cell that could cause bone destruction. The galvanic corrosion may be started due to the interaction of prosthetic devices. For example, a restoration or prosthesis in physical contact with amalgam in an adjacent tooth or between dental implants, fillings or crowns [9].
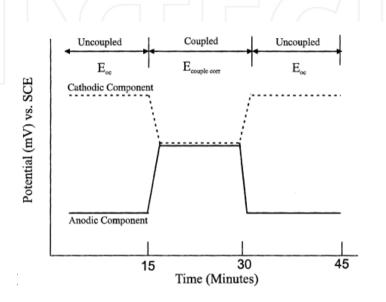

Figure 1. Schematic of data acquired during continuous potential measurement [8].

2. Methods

The measurement of the biocompatibility of dental alloys is a complicated issue. However, tests for biocompatibility assessment are classified as either in vitro or in vivo tests. In vitro tests are performed outside a living organism, while in vivo tests are conducted in an animal's body. In vitro tests are the cheapest and fastest of the biocompatibility tests, but because they are not performed in a living system, their significance is often subjected. Conversely, in vivo tests are more informative than in vitro due to the fact that the device is subjected to all dimensions of the biological response, but they are also expensive and highly complex to control and interpret.

In addition, biocompatibility is relatively related to other properties of the alloys such as corrosion having a direct relationship with the release of metal ions. The presence of metal

ions in the body may cause various phenomena such as transportation, metabolism, allergy, carcinoma and accumulation in organs. Therefore, measuring the metal ion release of bio-materials (dental alloys) is important as well as other biocompatibility tests, which is done by methods like atomic absorption spectroscopy, inductively coupled plasma mass spectro-scopy, or X-ray fluorescence spectroscopy.

Moreover, since the release of metal ions depends on electrochemical rules, many efforts made to evaluate the biocompatibility of dental alloys by corrosion tests in in vitro and in vivo studies. For this specific case, as was discussed earlier, galvanic corrosion can enhance the corrosion rate of the anode resulting in high amount of metal ion released. Zero Resist-ance Ammetry is the main method used to evaluate galvanic corrosion behavior of dental alloys; with ZRA probes, two electrodes of dissimilar metals are exposed to the process flu-id. When immersed in solution, a natural voltage (potential) difference exits between the electrodes. The current generated due to this potential difference relates to the rate of corro-sion which is occurring on the more active of the electrode couple. A schematic of the exper-imental setup is shown in Fig. 2. Besides, the measurement of currents and potentials in galvanic couple or uncoupled electrodes has been made to obtain more information. More-over, the electrochemical corrosion tests like open circuit potential, cyclic and linear polari-zation, potentiostatic polarization or electrochemical impedance spectroscopy (EIS) have been developed for many years to estimate the degree of corrosion on dental alloys by meas-uring the current flow during the corrosion process, or change in potential of the alloy rela-tive to some standard.
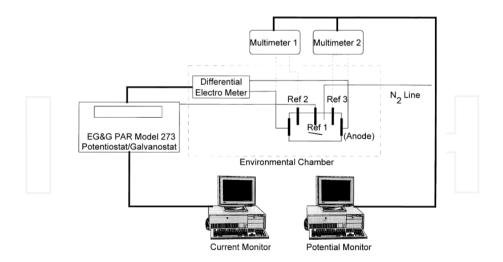

Figure 2. Schematic diagram for the galvanic cell set-up [8].

3. *In vitro* and *in vivo* tests

The aim of this section is to evaluate and compare, in vitro and in vivo, the galvanic corrosion behavior of dental alloys such as restorations, amalgam, implants or orthodontic materials when they are used in a mouth at the same time. It was indicated in the previous section that the simultaneous using of these devices can cause some biologic problems due to the galvanic corrosion effect.

Nowadays, titanium and titanium alloys are widely used in odontology because of their excellent characteristics such as good mechanical behavior, low density, high corrosion resistance in body fluids and excellent biocompatibility. The high biocompatibility of these alloys is attributed to the formation of the passive film (TiO_2) on the surface, which is highly protective. As these alloy implants and prosthetic devices become more common, the galvanic interaction with other metallic materials may become an issue [9, 11, 15, 16]. Studies of galvanic cells of titanium with dental alloys indicated either almost no interaction, or very small galvanic currents [11, 15, 17]. R. Venugopalan and L. C. Lucas [8] used continuous corrosion potential monitoring in coincidence with Zero Resistance Ammetry to achieve galvanic corrosion properties of restorative and implant materials coupled with titanium. All tests were carried out in artificial salvia solution. The composition of the electrolyte is shown in Table 2. They found that noble restorative (Au-, Ag-, and Pd-based) alloys coupled to titanium are least susceptible to galvanic corrosion, while the Ni–Cr–Be alloy showed unstable galvanic corrosion behavior. Also findings of N. M. Taher and A. S. Al Jabab [2] indicated that the highest galvanic corrosion resistant alloys coupled with titanium implant abutment material were Pontallor (Au-based), Ternary Ti, R800 (Co-Cr alloy) and Jelstar (Ag-Pd alloy), respectively. But, RCS (Ni–Cr) alloy was found to be highly susceptible to galvanic corrosion, which is in accordance with former study. In general, it should be mentioned that titanium was anodic to noble alloys and cathodic to iron and nickel-based passivating alloys. It is also worth noting that other researchers could obtain relatively similar results [11, 18].
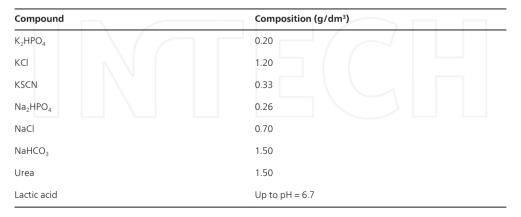
Compound	Composition (g/dm³)
K_2HPO_4	0.20
KCl	1.20
KSCN	0.33
Na_2HPO_4	0.26
NaCl	0.70
$NaHCO_3$	1.50
Urea	1.50
Lactic acid	Up to pH = 6.7

Table 2. Chemical composition of the artificial salvia

Dental amalgams are still the most common metallic direct filling materials. However, because of mercury toxicity, low-mercury and mercury-free gallium-based direct filling alloys have been developed in recent years. Both dental amalgams and gallium-based filling alloys are passivating materials with less protective passive film in comparison with titanium or most other passivating dental alloys. Researchers [9, 19] have considered the galvanic interaction between titanium and direct filling alloys like gallium and variety of copper containing amalgams. They reported that the galvanic interaction between titanium and direct filling alloys is small. The gallium alloy was the most sensitive to galvanic corrosion among the samples when in contact with titanium, which is ascribed to relatively poor corrosion resistance of gallium alloys [20]. It was shown that the galvanic corrosion resistance of mentioned alloys coupled to Ti from the highest to lowest are as follows: High copper dental amalgam > Low copper dental amalgam > Gallium-based direct filling.

Nitinol (Nickel titanium) is a very attractive material for use as an orthodontic wire due to its unique shape memory and superelasticity properties. Researchers evaluated the galvanic corrosion of these orthodontic wires with dental alloys in artificial saliva. They found that placing stainless steel brackets or Aristaloy (Ag-Cu-Sn) amalgam in direct contact to nitinol arch wire is not recommended, because it causes enhanced corrosion rate of nitinol arch wire. They also suggested that using ceramic brackets instead of stainless steel brackets could help to get rid of the occurrence of galvanic corrosion [21].

Another group of metals used in dentistry is chromium based alloys. Ciszewski et al. [4] investigated the galvanic corrosion behavior of Remanium GM 380 (chromium–cobalt alloy) and Remanium CS (chromium–nickel alloy) when bound together or coupled with Amalcap plus (silver-based amalgam) in an artificial saliva solution at 37°C. It was found that a bimetallic cell consisting of Remanium CS and Remanium GM 380 alloys has a very low EMF (electromotive force) which is not a potential source of galvanic currents in the oral cavity. Conversely, galvanic cells prepared from Amalcap plus and Remanium CS or Remanium GM 380 showed a much greater EMF. This obviously showed that in these latter it is possible to expect some metal ions in the saliva solution as a result of galvanic currents. They also indicated that even elements from a cathode specimen of a galvanic cell are able to dissolve into the solution. These results, from an electrochemical point of view, are surprising.

Since in vivo tests are generally expensive, time consuming, controversial and complex to study, there are few reports on the galvanic corrosion behavior of dental devices in a living organism. Most researchers have performed an indirect measuring technique to determine in vivo galvanic currents of dental alloys [22-24]. Palaghias et al. [25] investigated in vivo behavior of gold-plated stainless steel titanium dental retention pins and showed that in vivo corrosion resistance of the titanium pins was superior to that of gold-plated stainless steel pins. Besides, Nilner et al. [26] found that gold-gold couples have lower galvanic currents than those of amalgam-amalgam and amalgam-gold couples; they indicated that galvanic currents for the couples are generally below 15 mA, which is below the threshold of pain (20 mA) [13]. It should be mentioned that the galvanic corrosion behavior of dental alloys is expected to fluctuate over time due to various factors, including changes in the pH and composition of saliva, disruption of the alloy's passive film due to chewing, and aging

of the restoration. Changes may also take place because of thermal and mechanical stresses [10, 27, 28]. As a result, it is concluded that the interpretation of this type of test is so complicated and needs more time to investigate.

4. Parameters affect galvanic corrosion

One of the important factors affecting the galvanic corrosion is the surface area ratio of the two dissimilar alloys (cathode/anode). An unfavorable area ratio, which consists of a large cathode and small anode, may cause a higher corrosion [12]. Reports showed that the galvanic potential and current density increased with the increasing Ti/alloy area ratio, where Ti plays the role of cathode. Therefore, the higher galvanic corrosion occurred [9, 29]. Besides, reducing the surface area of the anode by 75 percent increases the galvanic activity of stainless steel/nitinol couple [30]. However, Iijima et al. found that the different anodic/cathodic area ratios (1:1, 1:2.35, and 1:3.64) had little effect on galvanic corrosion behavior of stainless steels and titanium bracket alloys coupled with four common wire alloys: nickel-titanium alloy, β-titanium alloy, stainless steel and cobalt-chromium-nickel alloy [31].

Fluoride is well known as an effective caries prophylactic agent and its systemic application has been recommended widely over recent decades to be the main method for preventing plaque formation and dental caries. Toothpastes, mouthwashes, and prophylactic gels contain from 200 to 20,000 ppm F(-) and can impair the corrosion resistance of dental alloys in the oral cavity [32, 33]. Anwar et al. [34] considered the effect of fluoride ion concentration on the corrosion behavior of Ti and Ti6Al4V implant alloys, when coupled with either metal/ceramic or all-ceramic superstructures. It was shown that increased fluoride concentration leads to a decrease in the corrosion resistance of all tested couples. Moreover, findings of Johansson and Bergman showed that adding fluoride to the solution made the titanium potential more active and enhanced the corrosion of titanium in combination with high-copper amalgams [29]. In fact, authors have exhibited that increase in concentration of NaF (fluoride ion) decreases the corrosion resistance of NiTi arch wires [35, 36] and titanium implants in different solutions [37, 38]. It is also demonstrated that the combination of low pH and presence of fluoride ions in solution severely affect the breakdown of the protective passivation layer that normally exists on nitinol and titanium alloys, leading to pitting corrosion [39, 40, 41].

Another parameter which could affect galvanic current is the initiation of localized corrosion (pitting and crevice corrosion). Mastication and other food contents (such as chloride ions) may initiate localized corrosion of dental alloys. This type of corrosion once initiated the corrosion current density and therefore the galvanic current increase. The presence of pitting on Nitinol arch wire harshly increases the galvanic corrosion rate of the anode, which indicates that dentists and researchers should be aware of other types of corrosion as well as galvanic one to investigate dental alloys appropriately. It was also mentioned that, initiation of localized corrosion on anode increased the galvanic current by up to 45 times revealing that consideration of the effect of localized corrosion on galvanic corrosion is necessary [21].

5. Preventing galvanic corrosion

According to the published literature and experimental results, the set-up for an acceptable couple combination in the mouth environment could be defined as the following: (1) the difference in $E_{o.c.}$ of the two materials and the $I_{couplecorr}$ should be as small as possible; (2) the $E_{couplecorr}$ of the couple combination should be significantly lower than the breakdown potential of the anodic component and (3) the repassivation properties of the anodic component of the couple should also be acceptable [8]. Besides, the use of some special composites, ceramics and metallic glasses can improve galvanic corrosion behavior of dental alloys. Metallic glasses, called also glassy or amorphous metals are rapidly quenched alloys explained as a metastable class of materials with no long range periodic lattice structure. These alloys are considered to be the materials of future [42, 43]. J.-J. Oak et al. [44, 45] developed new Ti-based bulk metallic glassy (BMG) alloys for application as biomaterials. Ti-based amorphous alloys containing no harmful elements (Ni, Al, Be) are expected to exhibit high potential for dental materials. The Ti-based amorphous ribbons exhibited good bend ductility, higher strength and lower Young's modulus than pure Ti and Ti–6Al–4V alloy. In addition, Ti-based amorphous alloys had an excellent potentiality of corrosion resistance that were passivated in wide passive range and at the lower passive current density in simulated body fluid conditions. It is demonstrated that the $Ti_{44.1}Zr_{9.8}Pd_{9.8}Cu_{30.38}Sn_{3.92}Nb_2$ bulk glassy alloy has a high potentiality to be applied in dental implant devices. These materials can be applied as coatings on the amalgams or restorative alloys to improve corrosion resistance of substrates.

6. Summary

In this review, we have highlighted comprehensive study of galvanic corrosion behavior of dental alloys. The titanium /titanium alloys, gold, silver-palladium and cobalt-chromium are main classes of alloys widely used as dental implants. In general, although they have exceptional properties which make them ideal for corrosion and wear resistance dental applications, it has been reported that failures of some implants are due to the galvanic-type corrosion. The galvanic current passes through the metal/metal junctions, which may finally cause pain owing to release of metal ions. The oral environment is particularly favorable for corrosion. The corrosive process is mainly of an electrochemical nature and natural saliva presents a good electrolyte. Fluctuations in temperature (hot and cold meals), changes in pH because of diet (milk products or acid dressings), and decomposition of food all contribute to the process. It is also mentioned that the parameters like the surface area ratio of the two dissimilar alloys, pH and the presence of fluoride could severely affect galvanic corrosion. To measure galvanic corrosion, researchers have investigated direct coupling or galvanic experiments which are conducted on restorative and implant materials coupled to another dental device like amalgam. They launched a comparative assessment of the electrochemical measurements attained using different methods and different preparation to study this type of corrosion. Zero Resistance Ammetry is the main method used to evaluate galvanic corro-

sion behavior of dental alloys in in vitro and in vivo. Besides, in this review, it is shown that new types of prosthesis/implants like metallic glasses (ribbons) could be applied as new generation of implants with excellent corrosion properties. These materials can be applied as coatings on the dental alloys to improve corrosion resistance of substrates.

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