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Corrosive failure of metals and alloys in dentistry: a review

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Abstract: In order to restore the normal functions of the dentition, metals and alloys are often a good choice for their desirable mechanical properties. Corrosion has been considered as the most important factor in the selection of metallic dental restorations, appliances, and implants, and one of the most common causes of failure. Although gold alloys have excellent biological response, their use has declined due to their high cost. Various types of dental alloys have replaced the inert gold alloys, such aloys sometimes show superior strength but less resistance to corrosion and degradation. Therefore, increasing knowledge about interaction of such dental alloys with oral tissues is mandatory. This includes understanding the alloy composition, interaction with possible agents present in the oral cavity, and different factors influencing their reactivity. The current review describes the different forms of corrosion that may occur in the oral setting, their consequences, and how to minimize their effect.

Keywords: *Corrosion; Dental Alloys; Biocompatability*

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A wide variety of metals and alloys are used in dentistry for restorations and prosthetic devices. Their successful clinical performance and long-term durability require adequate corrosion resistance in the oral environment [1].

Corrosion is the chemical reaction of a metal with components of its environment. Since the metals used in dental or biomaterials field may be exposed to wet, warm, salty, acidic and oxygenated conditions, the possibility of such reactions must be considered [2].

Tarnish is a surface discoloration on a metal or a slight loss of the surface finish or luster due to the formation of thin films, such as surface oxides, sulfides, or chlorides. Whereas **corrosion** is a process whereby deterioration of a metal is caused by reaction with its environment. Eventually, corrosion can cause severe and catastrophic disintegration of metals [3].

Passivity means that some normally active metals and alloys, lose their chemical reactivity and become extremely inert, as a result of formation of a highly adherent and very thin oxide film on the metal surface, which serves as a protective barrier to further corrosion. It occurs with particular metals, such as Chromium, Aluminum, and Titanium [4].

The oral environment is highly conducive to electrochemical action. Corrosive disintegration can take place through the action of moisture, temperature fluctuations, acid or alkaline solutions, and certain chemicals, such as sulfur and chlorine ions. Also, fluoride ions interfere in the titanium oxide formation which causes changes in the protective passive layer of the metal [5].

Fundamental Basis of Corrosion

The most commonly used metals naturally exist as compounds of various oxides or sulfides, such as Fe_3O_4, Al_2O_3, or CuS. These compounds (minerals) represent the thermodynamically stable form (lowest energy state). Pure metals are then extracted by metallurgical techniques. Thus, pure metals spontaneously react with oxygen, sulfur, or chlorine in order to revert to their lowest energy state, which is actually the process of corrosion. On the other hand, gold and other noble metals are found in their pure form (native state), so they do not corrode[1]. Essentially, corrosion occurs from two simultaneous reactions: oxidation and reduction (redox). The oxidation (anodic) reaction results in dissolution of the metal (M), and positive ions are produced ($M \rightarrow M^{2+} + 2e^-$). Reduction occurs at the cathode, with hydrogen ions reduced to hydrogen gas ($2H^+ + 2e^- \rightarrow H_2$) [6].

Corrosion of a metal is either a chemical or an electrochemical process:

Chemical (dry) corrosion is the direct combination of metallic and nonmetallic elements to yield a chemical compound through oxidation reactions, in the absence of water or another fluid electrolyte.

Electrochemical (galvanic/wet) corrosion requires the presence of water or some other fluid electrolyte and a pathway for the transport of electrons.

Forms of Electrochemical Corrosion

1. *Galvanic Corrosion*

This occurs when dissimilar metals, such as metal restorations with different compositions, are placed in adjacent or opposing teeth (Figure 1A): When brought into contact, there is a sudden short-circuit through the two alloys, that might result in a sharp pain, called galvanic shock. When the teeth are not in contact, there is still an electrical circuit associated with the difference in potential between the two restorations. These galvanic currents also occur between restorations of similar alloys (such as an old amalgam filling and a freshly placed restoration), which will never have exactly the same surface composition or structure. A current is present even in a single metallic restoration, although it is less intense (Figure 1B). The electrochemical cell is generated due to the electrical potential differences created by the two electrolytes: saliva and tissue fluids (the dentinal fluid, soft tissue fluid, and blood). Since the chlorine ion concentration is seven times higher than that of saliva, the interior surfaces of a dental restoration will have a more active electrochemical potential [1].

Another type of galvanic corrosion is associated with the **heterogeneous** composition of the dental alloys' surfaces, having differences in electrode potential. Examples: eutectic alloys, cored structure, impurities at grain boundaries, and solder joints [1].

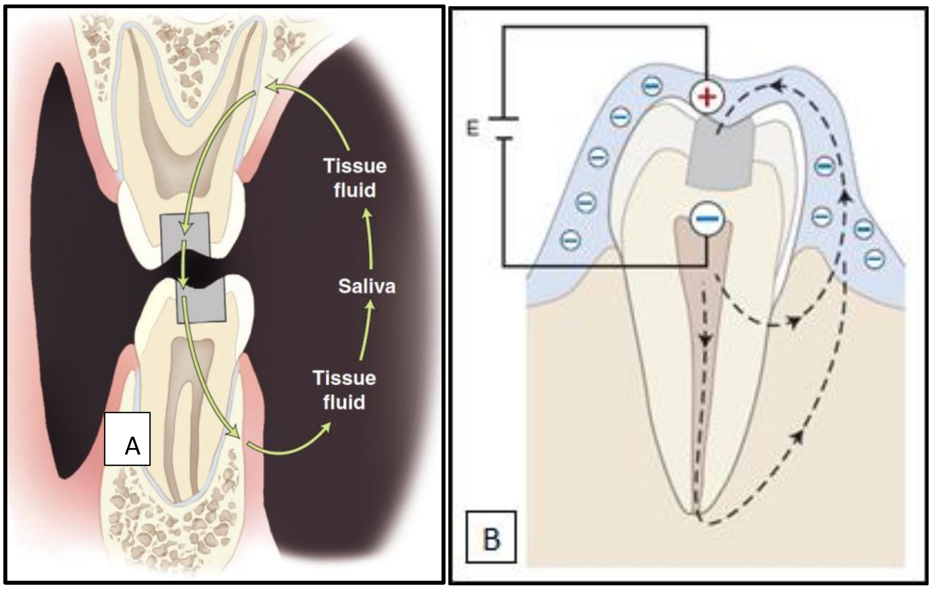

Figure 1. Electrochemical corrosion (A) in dissimilar metallic fillings, (B) in the same filling [1].

2. *Crevice Corrosion*

This occurs whenever there are variations in the electrolyte within the system, i.e: difference in composition (Figure 2). For example:

- Corrosion at interproximal areas due to food debris modifying the electrolyte composition, to be different from normal saliva.
- Irregularities, such as pits, scratches, and cracks, in restoration are covered by food debris and mucin, so the bottom of the defect is oxygen-deprived. Crevice corrosion results from differences in the **oxygen** concentration.
- **Pitting corrosion** is similar to crevice corrosion but it can be initiated on a relatively smooth surface, due to break in the passive layer. Pitting corrosion is caused by occlusal wear, or an environment with low pH, or aggressive chemical species such as chloride.
- Electrochemical testing of titanium implants and associated suprastructures showed crevice or pitting corrosion in the marginal gap and at the suprastructure surface [7].

The **rate** of such corrosion may be very rapid, since the area of the anodic region is much smaller than that of the cathode. This unfavorable anode-to-cathode ratio causes rapid corrosion known as **localized** corrosion. Consequently, failure may occur much more rapidly than would be expected from a **uniform** surface attack [1].

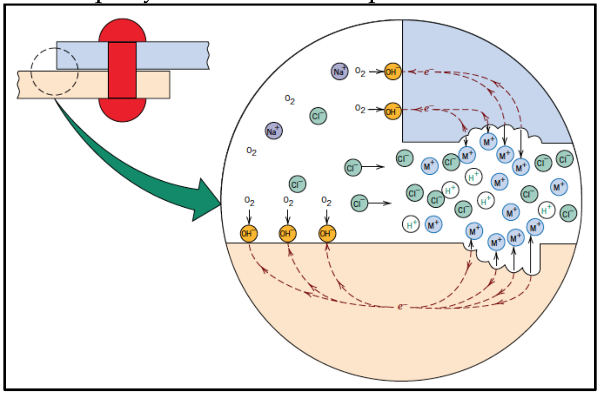

Figure 2. Schematic illustration of the mechanism of crevice corrosion [4].

3. *Intergranular Corrosion (Intercrystalline/Interdendritic)*

Disintegration occurs preferentially along grain boundaries for some alloys, in specific environments. This type of corrosion is common in **stainless steels** when subjected to prolonged heating between 500°C and 800°C (during heat treatment or welding). They become susceptible to intergranular attack due to formation of small precipitate particles of chromium carbide ($Cr_{23}C_6$) along the grain boundaries. This leaves a chromium-depleted zone adjacent to the grain boundary, which is known as **sensitization/weld decay**, this grain boundary region is now highly susceptible to corrosion (Figure 3) [4].

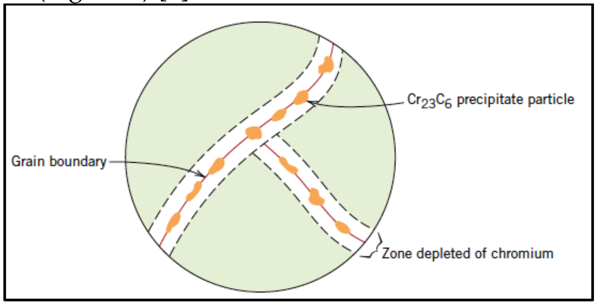

Figure 3. Schematic illustration of chromium carbide particle that have precipitated along grain boundaries in stainless steel, and the zones of chromium depletion [4].

4. *Selective Leaching*

Selective leaching is the removal of the less noble component of the solid solution alloy by a microscopic-scale galvanic corrosion mechanism. Examples: Zinc in brass (dezincification), Copper or Silver in Gold alloys, and Molybdenum in Nickel- Molybdenum alloys.

Two mechanisms were described for selective leaching:

(1) Two metals in an alloy are dissolved, and one redeposits on the surface (as in Zinc).
(2) Or one metal is selectively dissolved, leaving the other metals behind (as in Molybdenum) [4,8].

5. *Erosion–Corrosion*

Erosion–corrosion arises from the combined action of chemical attack and mechanical abrasion or wear as a consequence of fluid motion.

Metal alloys are susceptible to erosion–corrosion, especially alloys that passivate by forming a protective surface film; the abrasive action may erode away the film, leaving exposed a bare metal surface. If the coating is not capable of continuously and rapidly re-forming as a protective barrier, corrosion may be severe[4]. The combination of a corrosive fluid and high flow velocity results in erosion-corrosion of dental titanium implants [7].

6. *Stress Corrosion*

Stress can accelerate the corrosion process, since the internal energy is increased. Stress is either externally applied or residual stress:

- When permanent deformation occurs in **cold-worked** structures.
- Atoms at the **grain boundaries**, which have higher energies.
- For most metallic dental appliances, stress corrosion is most likely to occur during **fatigue or cyclic loading**. Small surface irregularities act as sites of stress concentration so the effects of fatigue and corrosion are combined [1,9].

7. *Hydrogen Embrittlement*

Various metal alloys, specifically some steels, experience a significant reduction in ductility and tensile strength when hydrogen, in its atomic form (H), penetrates into the material, and diffuses interstitially through the crystal lattice. When these hydrogen atoms re-combine in the voids of the metal matrix to form hydrogen molecules, they create internal pressure leading to crack formation (hydrogen induced cracking). Also, cracking may be due to interference of dislocation motion by the formed hydrides [4].

On the other hand, hydrogen interaction with titanium takes the form of a simple eutectoid transformation with the α + hydride phases forming directly from the β phase [10].

8. *Microbiologically-Influenced Corrosion 'Biocorrosion"*

It is defined as the deterioration of the metal surface due to the direct or indirect activity of living microorganisms [11].

Sulfate-reducing bacteria are the most important anaerobic bacteria that influence the corrosion behavior of steels, Co-Cr-Mo and Ti-6Al-4V alloys [11,13]. These bacteria reduce inorganic sulfates to sulfides in the presence of hydrogen according to the equation:

$$SO_4^{2-} + 8H \rightarrow S^{2-} + 4H_2O$$

Hydrogen is provided by the cathodic reaction or in the general environment. Iron, for example, reacts with sulfides as follows:

$$Fe^{2+} + S^{2-} \rightarrow 2FeS$$

The presence of iron sulfide in rust is often an indication that corrosion was influenced by sulfate-reducing bacteria (Figure 4)[14]. Moreover, studies showed that Streptococcus mutans and Streptococcus sanguinis species were able to corrode various orthodontic appliances [15].

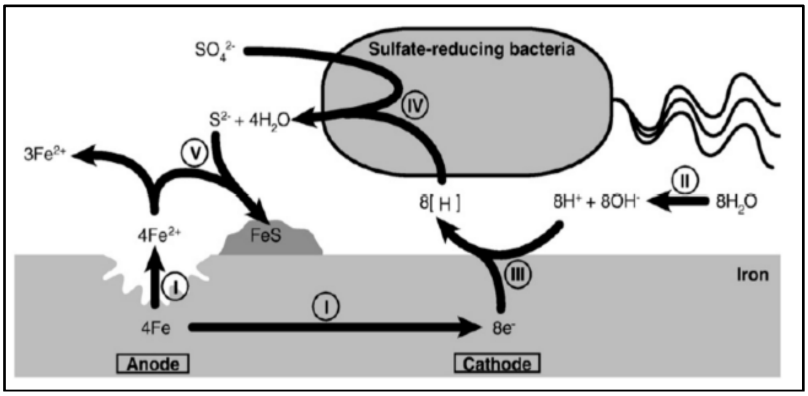

Figure 4. Schematic illustration of microbiologically influenced corrosion (MIC) for sulphate-reducing bacteria (SRB) at an iron electrode [16].

Furthermore, oral bacteria might **indirectly** contribute to corrosion of metallic restoration: the aqueous environment of the oral cavity fosters adhesion of bacteria to metal surfaces and formation of biofilms. It was also stated that the activity of sulfate reducing bacteria causes a difference in potential between surfaces in contact with bacteria, and other surfaces not in contact with bacteria, which leads to the formation of crevice/pitting corrosion [14].

9. *Fretting Corrosion / Tribocorrosion*

Fretting corrosion is **wear**-assisted corrosion, in which the tribological load leads to local mechanical destruction of the passive film. It is considered the dominant failure mode in Titanium orthopedic implants. Even though a spontaneous repassivation reaction takes place in many cases, continuous activation/ repassivation cycles lead to an increased material loss [17].

Undesirable Effects of Corrosion

Corrosion of any kind is usually undesirable; it has several possible consequences:

- Small galvanic currents associated with corrosion can cause sharp transient postoperative **pain**, known as galvanic shock. Such pain usually occurs immediately after insertion of a restoration and subsides in a few days.
- Metallic **taste** might also be experienced by the patient due to release of ions.
- The metals commonly used are those from the transition periods of the table of the elements. Their oxides and salts are typically strongly colored. Thus, their corrosion products will tend to **discolor** the metal itself, or the surrounding tissue or other materials.
- The fact that metal is being removed from the surface of the object by the corrosion reactions means that its **roughness** may increase. This would spoil the appearance of the highly polished metallic object, also, it would be more retentive of plaque.
- The extensive loss of material from intergranular spaces or in pitting, may reduce the **mechanical** strength of the object, causing failure[18].
- The 'heavy' metals are mostly **toxic**, corrosion products therefore may pose a threat of local or systemic effect on the organism [2].

The main factors which affect rate of corrosion are

1.More the reactivity of metal, the more will be the possibility of the metal getting corroded.
2.The impurities help in setting up voltaic cells, which increase the speed of corrosion.
3. Presence of electrolytes in electrolyte also increases the rate of corrosion.
4. A rise in temperature (within a reasonable limit) increases the rate of corrosion.
5. Unfavorable anode-to-cathode ratio leads to faster corrosion rate "localized corrosion" [1].

CONCLUSION

Being in a highly interactive oral environment, the biocompatibility of dental alloys is sometimes questionable. Modification of composition and optimization of application conditions are a must in order to ensure high performance of metallic appliances and desirable patient safety.

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