Dental Alloys and Corrosion Resistance

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Summary

Metals and their alloys are unavoidable materials in everyday dental use for the making of fillings, cast cores and post systems, individual crowns, implantants' suprastructures, dentures and orthodontic devices. Materials implanted in the mouth are exposed over a long period of time to functional, biochemical and bacterial influences of a mouth media which can have a negative impact on a very therapeutic work or surrounding tissue. Corrosive resistance is a prerequisite for biocompatibility. Due to economic reasons, corrosive resistant precious metals have been used less frequently, while the non precious alloys appear on the market. Since a dentist is responsible for a choice of implanted metal, prior to implantation it is important to foresee the impact of saliva as an aggressive media on a metal or alloy. Based on studying different literature, the purpose of this work was to give and overview of the existing dental metals and alloys in contexts with their anticorrosive characteristics, and that way to help a dentist in making a right choice.

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Introduction

Today a number of different alloys are used in dentistry for fillings, fixed and mobile prosthetic works, orthodontic devices and dental implants. Applied alloys in a mouth are exposed to the influence of chemical, biological, mechanical, thermal and electrical forces. These forces have a negative effect on functional and esthetic characteristics of dental works and they substantially lessen their durability. Electrochemical corrosion (1) is the most important damaging factor of dental works. Corrosion is the unintentional wearing down of the metal surfaces, and damage to the outer and inner layers of their surface caused by exposure to chemical or electrochemical reaction of the surrounding area (2). Electrolyte is needed for electrochemical reaction. Saliva, as well as soft and a hard tissue, has the role of electrolyte in the mouth. Saliva is a media of strong corrosive affect. The corrosion potential of saliva increases as its pH factor decreases and as chloride concentration increases (3). In most alloy--electrolyte systems, corrosion stops on the very surface by creation of a surface oxide layer which is good protection from further corrosion. Two different protective layers are formed in the mouth: an oxide layer and a biofilm.

Oxide layer and biofilm

If we dip one or more metals in the mouth, the metal tends to ionize. Because of the difference in alloy potentials, alloy ions tend to convert to electrolyte and by this action metal melts. By absorption of oxygen an oxide film is formed on the surface of the alloy which prevents further melting of the rest of the alloy's components.

Biofilm is a surface layer that covers all surfaces in the mouth, and is formed by precipitation of proteins and glycoproteins from saliva. Therefore, the corrosive endurance of dental alloys depends on the chemical component of saliva, first and foremost the organic components (4). Biofilm influences the ion conversion between the alloy surface and the surrounding area (5). The most frequent is sulfide biofilm, which forms as a result of silver or copper sulfide formation. These are reactions of alloys and sulfur from food and drinks, and they cause alloy discoloration and decrease its further corrosive activity.

In spite of the oxide layer and biofilm formation, corrosion in the mouth continues. Because of the constant circulation of saliva, melted ions react in contact with new saliva and alloy releases the new ones, which provoke further corrosion. Lian and Meletis (6) proved in their investigations that dental works exposed to strong friction forces during mastication, corrode and weaken faster than those with less friction forces. They explained this by removing the passive oxide layer on the surface of the alloy during mastication. By removal of the new layer, the alloy wears down still more and deeper layers of alloy are affected by corrosion, which results in a weakening of the total work.

Dental alloys and corrosion resistance

Due to economic reasons, non-precious dental alloys are used more frequently. These are mostly Co-Cr and Ni-Cr alloys which are considerably cheaper than gold. They have higher tensile strength, their modul of elasticity is higher and they have less density. The negative characteristics in comparison with precious alloys are: the higher melting point, harder to shape, higher loss of shine and inclination to oxidation and corrosion. Also, Ni alloys frequently provoke allergic reactions. Application of these alloys in the mouth results in discoloration, a metal taste and resorption of damaging corrosive products through the gastrointestinal tract. Due to this fact, it is important to study the corrosive resistance of alloys containing nickel. Messer and Lucas (7) investigated different nickel alloys. Some of the alloys showed a high inclination towards corrosion and cytotoxicity, although such results were not shown by all nickel alloys. Özdemir and co-workers (8) investigated the quantity of released ions from Ni-Cr alloys Wirolloy and Wiron 99 dipped into a corrosive bath. Both alloys showed inclination towards corrosion, although Wironit released considerably less Ni and Cl ions than Wirolloy.

In spite of the allergic reactions to nickel, new Ni-Cr alloys, for example Wiron NT, have been marketed (9). Investigators on corrosion have shown that Wiron NT is an alloy of satisfactory corrosive resistance. The daily released quantity of Ni and Cr ions is less than the daily intake through food. Furthermore, it has been proved that the patients with confirmed allergy to Ni, have in their mouth prosthetic works made of Ni-Cr alloys and do not have any symptoms of allergy.

Pd is also an allergen. Pd-Cu alloys show allergic reactions, while such symptoms do not show with other Pd alloys (10). Berzins and co-workers (11) confirmed clinical results by a higher tendency towards corrosion of Pd-Cu alloys than other Pd alloys.

Angellini (12) demonstrated on Pd dental alloys that identical alloys in the same corrosive media can show a different tendency to corrosion, depending on technical conditions, for instance temperature and melting duration, reheating, cooling period and so on. The presence of fluoride in saliva can also increase the tendency to corrosion. Guglielmino (13) showed that the presence of NaF in saliva does not change corrosive activity of Pd alloys, but increases the corrosion of titanium alloy.

Hässler (14) investigated the corrosion endurance of a build-up of different chemical composition. After 1, 3, 7, 42, and 84 days left in an artificial saliva, the highest corrosion stability was shown by precious metals and titanium build-ups. CoCr alloys showed less stability. The first day FeCrNi alloys showed high corrosive instability, but after a passive phase, these alloys showed a satisfactory level of corrosive stability.

Hermann (15) investigated the affect of saliva's different pH on the hardness of Ni-Cr, Co-Cr and Pd alloys. He came to the conclusion that after 90 days left in a corrosive bath pH=4.2, the hardness of the majority of samples approached zero, while only Pd alloys showed somewhat better results.

Attachments are frequently connected onto a basic element by soldering or laser welding. Solders are alloys that can, depending on their chemical composition, corrode and shorten the usage of a total prosthetic work. Zak and Strietzel (16) warn of the importance of solders used because of their corrosive resistance, and they give the priority to laser welding.

Titanium

Due to its electrochemical characteristics, titanium, as the most biocompatible metal, is frequently used in modern dentistry-in implantation as well as in prosthetics (17, 18).

Marinovic (19) and co-workers investigated the corrosive resistance of titanium alloys for orthopedic implants in body liquids. Spectro-electrochemical researches of titanium alloys *in vitro* have showed the formation of quality protective oxide film on the alloy surfaces (20). Comparing the stability of titanium in different corrosive baths, with the results obtained with other alloys, the authors conclude that titanium has undoubtedly the highest corrosion resistance (21-24). However, in combination with different metals, it can form strong galvanic cells, so caution is necessary when combining titanium with other alloys. Some authors belive that precious metals (An, Ag, Pd) in combination with titanium practically do not form galvanic currents, while in combination with Cr-Mo and Ni-Cr, weak galvanic currents are formed. In combination with Ni-Cr-Be these currents are important, so those alloys have to be avoided. Venugoplan (25), however, considers these currents as unimportant.

Karen (26) investigated the influence of amino acids on titanium alloys corrosion and came to the conclusion that the presence of triptophan in saliva does not affect the corrosive resistance of titanium, while cistein raises it.

Biocompatibility and corrosive resistance

Alloy biocompatibility is closely linked with corrosive resistance (27-29). The damaging influence of alloy on the organism starts with the dissolving of its toxic components, which occurs as a result of corrosion. The negative impact of corrosion on dental alloys has been studied by various authors. These are mainly in vitro studies, that lack specific circumstances to which the alloys are exposed in the mouth, and that, according to the ADA does not provide completely reliable data (30).

Although many dental alloys do not have a high corrosive resistance compared to titanium, this does not mean that they should not be used. If one compares the toxic level of a certain element with the quantity that dissolves daily in the mouth as a result of corrosion, quite often one would have to wait for the whole crown to dissolve in order for a toxic dose to be released. Thus Strietzel (31) suggested a more comprehensive examination of conventional dental alloys corrosion, prior to abandoning their use. Precious alloys can also be corrosive, although much less than the non precious ones. After measuring the concentration of Pt and Au in the urine after implantation of prosthetic works made out of gold and platinum alloys, a considerably higher percentage of dissolved Pt ions was found, than that of Au ions (32). Several investigations have attempted to find a solution on how to produce nonprecious alloys that are corrosively more stable in a chemically aggressive media (33-36). By adding Pd and Au to an alloy, the corrosive resistance of Ag-Mn alloy is increased.

By adding Pd to the same alloy the corrosive decrease is considerably greater than by adding Au (37). Syverud and co-workers (38) showed *in vitro* that by adding Cu to a Pd alloy its corrosion increases, as well as its cytotoxicity. This is also proved by the clinical results of the appearance of gingivitis around the implanted alloy. Wataha and Lockwood (39) investigated the corrosion resistance of Au, Ag, Pd and Ni alloys, and proved that Au-Pd alloys have the highest corrosive resistance, while Au-Ag-Cu alloys have the lowest.

A higher level of corrosive resistance in nonprecious alloys could be achieved by covering them with protective layers (40-43).

Anticorrosive protective films and dental alloys

Co-Cr alloys plated with a thin ZrO_2 layer showed a considerable increase in corrosive resistance, as well as good quality of bonded hardness between the alloy and film, and for that reason they were recommended for widespread use by the authors Hsu and Yen (44). New, amorphous corrosive resistant alloys came on the market which could also be used for protection against dental alloys corrosion (45-47). By the appearance of corrosive resistant amorphous Fe-Cr-P-C alloys in 1974 different amorphous corrosive resistant alloys came on the market (48-50). Investigations on amorphous Al-W alloys have shown that these alloys have good electric and chemical characteristics, and high resistance to crystallization and change in temperature. According to studies done in HCL solution and artificial saliva, a high level of corrosive resistance has been found, which has been in correlation with the chemical composition of the alloy, i.e. the percentage of Al and W in the alloy.

It is considered that by usage of such protective films, corrosive nonresistant non precious alloys could be satisfactory in replacing expensive precious alloys (51, 52).

Conclusion

The corrosive resistance of metal is its important characteristic during implantation into a mouth. Therefore precious alloys are the most suitable for dental use. However, due to economic reasons, nonprecious alloys are frequently used. Because of its physical-chemical characteristics, titanium has been the material of choice during the implantation of nonprecious alloys. By plating nonprecious alloys with corrosive resistant alloys, the choice of implanted nonprecious alloy could also spread to other economic alloys. Investigations have been performed on different coatings which together with anticorrosive characteristics have other corresponding ones and this way find widespread clinical usage.