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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].

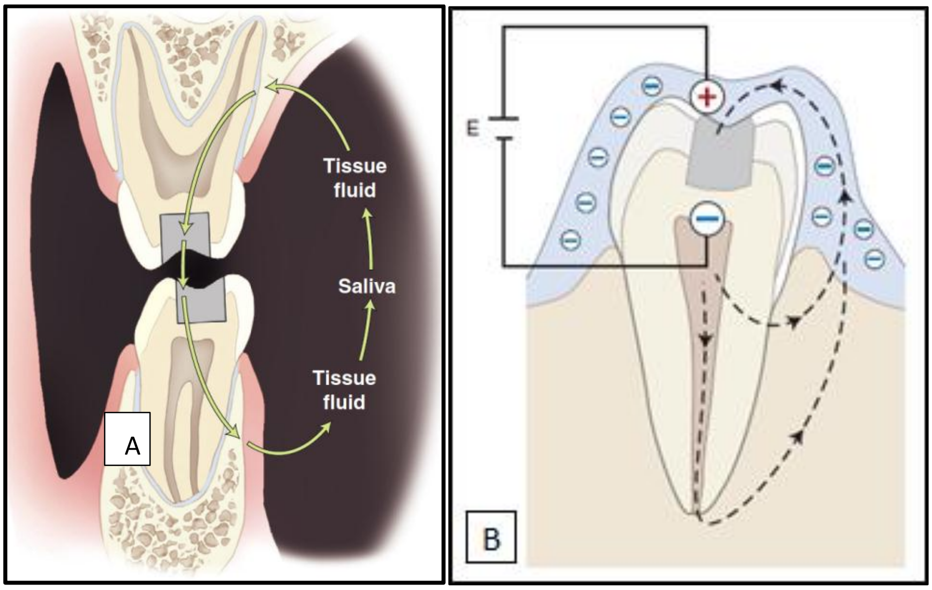

Figure 1. Electrochemical corrosion (A) in dissimilar metallic fillings, (B) in the same filling [1].

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].

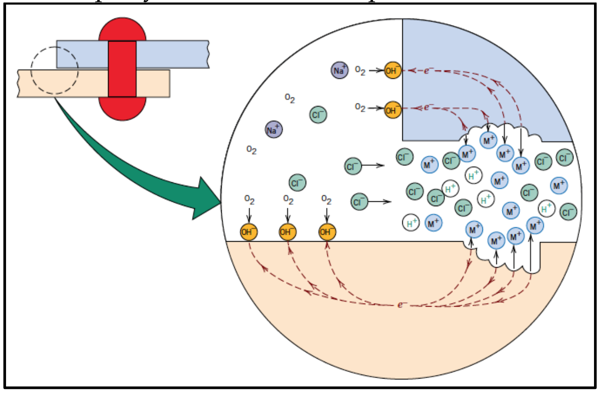

Figure 2. Schematic illustration of the mechanism of crevice corrosion [4].

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].

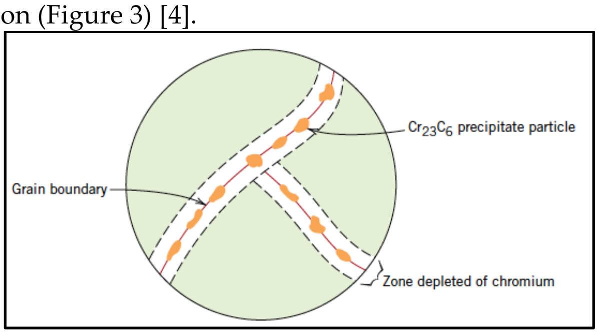

Figure 3. Schematic illustration of chromium carbide particle that have precipitated along grain boundaries in stainless steel, and the zones of chromium depletion [4].

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].

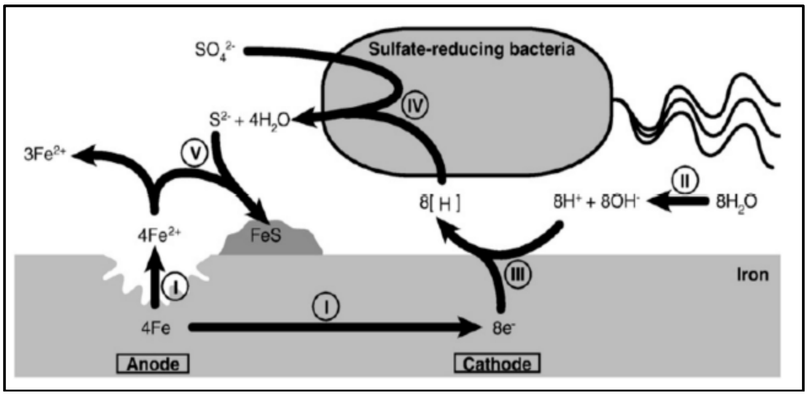

Figure 4. Schematic illustration of microbiologically influenced corrosion (MIC) for sulphate-reducing bacteria (SRB) at an iron electrode [16].

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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Introduction to Drug Delivery Systems

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Abstract: A wide range of drug delivery systems has been applied to accommodate the needs of regenerating oral tissues. Cells that are responsible for tissue regeneration may be either delivered via biomaterial carriers or recruited in vivo by signaling molecules.

Keywords: *Drug; Delivary.*

A wide range of drug delivery systems has been applied to accommodate the needs of regenerating oral tissues. Cells that are responsible for tissue regeneration may be either delivered via biomaterial carriers or recruited in vivo by signaling molecules. (1)

Drug delivery by controlled release provides several critical advantages because bioactive factors are transported to the desirable milieu in biocompatible carriers, released in a controlled manner and may locally regulate multiple processes of cell chemotaxis, attachment, proliferation, differentiation, and morphogenesis. In the absence of drug delivery and controlled release, bioactive factors may undergo rapid diffusion and denature shortly after in vivo delivery, and often fail to induce the intended effects on target cells and tissues. Although control released drugs or bioactive factors may also diffuse and denature, the continuous dosing provides sustained effects where subsequent doses act on cells that have already been sensitized by previous growth factor exposure. The bio-resorbable drug delivery systems should degrade into products that can be eliminated from the body through natural pathways or, even better, which are involved normally in metabolic pathways. (2)

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Example: For treatment of ***periodontal disease***, there is a need for an optimal local drug delivery system since the widespread systemic administration of antibiotics might cause undesired side effects or favor the development of resistances. The use of antibacterial biomaterials becomes increasingly important in medical and dental science. Especially in the field of conservative dentistry, the elimination of bacteria and plaque is foundational for effective treatment. (3)

For instance, the conventional treatment of ***periodontitis*** by scaling and root planning is advantageously accompanied by the adjuvant administration of antibiotics. Antibacterial drug compounds can be applied by systemic or local administration. Compared to systemic drug delivery the local administration of drugs in periodontology is considered to be more effective, since the pathogen-specific drug can be placed directly in the periodontal pocket achieving effective concentrations. In addition, the risk of undesired side effects caused by high systemic doses or resistance development can be reduced. (3)

For effective elimination of pathogenic bacteria, the antibiotic agent has to be available in the periodontal pocket in adequate concentrations for a sufficiently long period of time. It is therefore necessary to use local delivery systems that control the release of their agents and guarantee lasting drug concentrations in the pocket in spite of high sulcular fluid rates. (3)

Non-resorbable drug carrier systems is time consuming and their removal is required this incurs the risk of tissue damage. Thus, many resorbable drug delivery systems were developed during recent decades, such as drug loaded hydroxypropylcellulose films, which were first described by Noguchi et al. in 1984, or drug carrying gels such as Elyzol® (Dumex GmbH, Bad Vilbel, Germany) dental gel, based on melted glycerol mono-oleate. However, also for these systems, the periodontal milieu often poses the major problem that the required period of drug exposure (7–10 days) cannot be achieved. Also in the field of periodontal surgery – as in the transplantation of a mucous membrane– resorbability of the scaffold material is important to avoid inflammatory effects and surgical removal. Polylactide fibers containing the antibiotic metronidazole were also generated. (3)

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Type of the Paper (Mini-Review Article)

Shape Memory Alloys

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Abstract: Shape memory alloys (SMAs) are set apart from other metals by the fact that they are able to undergo a solid-to-solid phase transition. This ability enables them to assume two different crystalline lattice structures (martensite and austenite), depending on both the applied stress and the temperature.

Keywords: *Shape; memory; alloy*

The ***first observation*** of the shape memory effect in materials occurred in the 1930's. A Swedish physicist *Arne Olander* (1932) discovered an interesting phenomenon when working with an alloy of gold (Au) and cadmium (Cd). The Au- Cd alloy was plastically deformed when cool and upon heating it returned to original or 'memorized' dimensional configuration. This phenomenon was called the Shape Memory Effect (SME) and the alloys that exhibited this behavior were called Shape Memory Alloys (SMA). Greninger and Mooradian (1938) observed the formation and disappearance of a martensitic phase by decreasing and increasing the temperature of a Cu-Zn alloy. Further research revealed other materials that also demonstrated this phenomenon. In 1962, the shape memory properties of Nickel Titanium alloys were discovered by accident at the US Naval Ordnance Laboratories and patented Nitinol (1).

Shape memory alloys (SMAs) are set apart from other metals by the fact that they are able to undergo a solid-to-solid phase transition. This ability enables them to assume two different crystalline lattice structures (martensite and austenite), depending on both the applied stress and the temperature (1).

Martensite is the crystallographic description of the low temperature phase of a SMA, which starts to form during cooling. This is because the martensitic crystalline structure is thermodynamically more stable below a certain transition temperature. Martensite evolves from austenite crystals in various directions and can therefore have many different lattice arrangements, depending on the local stress field. Also the structure can appear as twinned or de-twinned. It is in this phase that a SMA can be deformed easily, because the molecular arrangement can easily change to a lattice arrangement that is more favorably aligned with the local stress field. This is mainly due to the mobility of the twinned boundaries (1).

Typically, a ***phase transition*** is induced by a change in temperature. The temperature at which the SMA starts to transform into the martensite phase is the martensite-start temperature (Ms). This transformation is completed when the temperature gets below the martensite-finish-temperature (Mf) (1).

The second crystalline lattice structure is ***austenite***, which is the strong, high temperature phase of a shape memory alloy. The molecular arrangement of the austenite structure is cubic and it is because of this symmetrical structure that the alloy shows a high modulus of elasticity. This austenitic structure is much stronger than the martensitic structure.

The ***phase transition*** is again induced by a change in temperature. The austenite phase starts to form out of the martensite phase at the austenite-start-temperature (As). This transformation is completed when the temperature gets above the austenite-finish-temperature (Af). However, above the Af temperature, the transformation of austenite to martensite can also be induced due to an applied load. This is called Strain Induced Martensite (SIM). This SIM is the working principle behind the superelastic Effect. The specific transformation temperatures can vary significantly, depending upon the exact chemical composition of the SMA (1).

To summarize, transformation between the martensite and austenite forms can be induced by both temperature and stress. Martensitie is the low temperature, high-stress form and austenite is the high-temperature, low-stress form. (2)

As result of this solid-to-solid phase transition, SMAs are able to show three special properties: the Shape Memory Effect, Martensitic Deformability and the Superelastic Effect (1).

Shape Memory Effect

The term Shape Memory Effect (SME) refers to the ability of SMA, which has been 'plastically' deformed, can recover a 'memorized' shape by heating it enough to complete the solid-to-solid phase transition. During this shape recovery, a SMA element is able to generate a great amount of work (1-3).

Thus, SMA elements recover a 'memorized' or predefined shape by heating the element above a certain temperature. The predefined shape is the shape that is given to the element upon fabrication at high temperatures, thus with the SMA being in its austenitic state. This effect is based on the solid-to-solid phase transition of SMAs that takes place within a specific temperature interval (1-3).

If the temperature of a SMA element is cooled below the Mf temperature, the SMA will be completely in the martensite phase, in which it can be easily deformed. After an obvious 'plastic' deformation, the element will remain deformed as long as the temperature stays below the transition temperature (the SMA stays in the martensitic phase). However, if the element is heated above the Af-temperature the structure of the SMA will return to its austenite state, which is configured in the original shape of the wire. Because of this the element will recover its original 'memorized' shape (1-3).

Furthermore, if this shape recovery is obstructed by an external mechanical component, a SMA element is able to generate very high forces and large amounts of work during the phase transformation. That is why SMA elements can be useful for actuating purposes in a variety of applications (1-3).

The SME can now be divided into two groups, the one-way and the two-way effect:

One-Way Effect

If a SMA element is deformed when it is in its martensitic state, this will result in the de-twinning of the differently orientated martensite structure. Similar to ordinary plastic deformation, the SMA element will stay in this deformed shape when the load is removed. However, upon heating the material will transform from the martensite to the austenite state and it will return to its original, 'memorized' shape. During this shape change the SMA element is capable of providing a significant amount of work output. If the element is subsequently cooled to its martensitic phase, it is normally not subjected to a reverse shape change, as long as there is no external stress during this transformation from austenite to martensite (1-3).

Two-Way Effect

A special form of the SME, in which not just the heating but also the cooling of a SMA element gives rise to a shape change, is called the two-way effect. SMA elements that possess this two-way effect are not only able to 'remember' a high temperature, austenitic shape, but also a low-temperature, martensitic shape. Because of this ability a SMA element is able to switch between these two shapes, depending on the temperature. Special thermomechanical treatment induced could this effect (1-3).

Martensite Deformability

A SMA element is very pliable when it is in the martensitic phase. This means that it can be bent over and over without strain hardening occurring and therefore with a much lower the risk of fracture than conventional materials. The reason for this is the twinned structure of the martensite structure. The twin boundaries can be moved very easily and without the formation of dislocations, which can be considered as the initiators of fracture. This property is called Martensite Deformability. Furthermore, the original shape can also be recovered after deformation when the element is heated. This is achieved by means of the Shape Memory Effect (1-3).

Superelastic Effect

In elastic deformation of typical materials a load will result in deformation that will disappear again upon removal of this load. The difference between this typical elastic deformation and the superelastic deformation, which occurs in SMAs, is that these can be stretched or compressed elastically ***5-10 times*** the amount of conventional materials. This is called the superelastic effect (termed pseudoelasticity in engineering material science). This effect can be observed at temperatures above the temperature necessary to transform the SMA from martensite to austenite (Af). To demonstrate the PE, the alloy chemical composition should be adjusted such that this transformation temperature corresponds with ambient temperatures in which the SMA is intended to be used (1-3).

Unlike the Shape Memory Effect, the superelastic Effect occurs without the need for a change in temperature. This is because the solid-to-solid phase change, which is the cause of the special properties of SMAs, can also be induced by the ***application of a load***. When a SMA element is loaded, while being in the austenitic phase, the initial behavior is elastic in nature. If the load is increased to a certain extent, the austenite structure transforms into martensite, simply due to the loading. This process is called a stress induced martensite (SIM) transformation. If this transformation is complete, the material will start to deform elastically again, as the stiffness of the martensite phase is much less than that of the austenite phase (1-3).

If the ***loading is removed*** before plastic yielding of the material, the material will unload elastically until the stress is low enough to start the transformation back into the parent austenite phase. This is possible because the temperature of the element is kept above the transition temperature Af at all times. If the stress is reduced even further, the material will complete its transformation back into its austenite phase and will continue to unload elastically until the zero stress point is reached. During this unloading process the SMA element can recover all of its induced strain and recover its initial, undeformed shape at zero stress (1).

There is energy dissipation taking place during the phase transformations from austenite to martensite and vice versa (***hysteresis***). The amount of dissipated energy is proportional to the extent of transformation completed during the loading cycle for both complete and incomplete, or partial, transformations. These partial transformations, the SMA is then composed of both the austenite and martensite phase at the same time, are also referred to as ***minor loop hysteresis cycles*** (1-3).

Nitinol in dentistry

The nickel-titanium alloys used in dentistry is 55 wt % nickel and 45 wt % titanium and possesses a temperature transition range. Cobalt is added to lower the temperature transition range. The austenitic NiTi phase has body centered cubic structure, and the martinstic NiTi phase has monoclinic, triclinic or hexagonal structure. In addition, a third form, called the *R phase* (rhombohedral) appears as an intermediate phase during the transformation. Compositional variations lead to changes in the martensitic and austenitic start and finish temperatures and mechanical properties. Thus, a number of variations of the Ni-Ti alloy have been developed in dentistry (2).

Mechanical properties of an ***orthodontic*** nickel titanium alloy are compared with those of stainless steel and a beta-titanium alloy. The nickel titanium alloy has the highest spring back (maximum elastic deflection) which is important if large deflections are needed, such as with poorly aligned teeth. Nickel-titanium has the lowest spring rate and the highest resiliency of the three alloys used for orthodontic wires. Clinically, the low elastic modulus and high resiliency mean that lower and more constant forces can be applied with activations and an increased working range.(18) The NiTi wire made from martensitic alloy, transformed to austenitic structure at body temperature (37° C), may exhibit the shape memory effect. The shape memory wires have superior springback compares to the superelastic one, thus used extensively in orthodontics (2).

On the other hand, since only those wires with austenitic finish temperatures less than 37° C exhibit superelasticity, therefore, ***endodontic instruments*** alloys have austenite-finish temperature being approximately 25 °C (2). Super-elastic files provide benefit by maintaining close contour to the canal shape without concern of file breakage (5). When the instrument is used in the canal, transformation from austenite to martensite occurs. Note the modulus of Ni-Ti austenite is 120 GPa, and that of martensite is 50 GPa. When the stress decreases, springback occurs without permanent deformation and a return to the austenitic phase. The super-elasticity of Ni-Ti permits deformations of 8% strain in endodontic files with complete recovery. This value compares to less than 1% with stainless steel instruments. In addition, the Ni-Ti alloys have lower moduli of elasticity than stainless steel, advantages in preparing curved root canals (4) .

However, the nitinol wire faces some ***difficulty in shaping***. The orthodontic nitinol wire requires special bending techniques and cannot be bent over a sharp edge or into a complete loop; thus the wire is more suited for use with pre-torqued, pre-angulated brackets. In addition, the alloy cannot be soldered or welded, so wires must be joined mechanically. (2) While, the nickel-titanium endodontic instruments must be fabricated by machining the starting wire, in contrast to stainless steel endodontic instruments in which a special apparatus is used to twist the starting wire (4,5).

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Smart Restorative Materials

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Abstract: Dentistry underwent rapid changes in the last decade with increased awareness for esthetics. Thus, tooth colored restorative materials become more and more important for daily practice. Metal-ceramic fixed restorations have been used with predictable longevity. However, this metallic base has a negative influence on the esthetic properties representing a real challenge. As a consequence, all-ceramic restorations do mimic better the natural tooth-esthetics.

Keywords: *Smart; restorative; Materials*

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Dentistry underwent rapid changes in the last decade with increased awareness for esthetics. Thus, tooth colored restorative materials become more and more important for daily practice. Metal-ceramic fixed restorations have been used with predictable longevity. However, this metallic base has a negative influence on the esthetic properties representing a real challenge. As a consequence, all-ceramic restorations do mimic better the natural tooth-esthetics. (1)

1- Smart Ceramics

In 1995 the first "all ceramic teeth bridge", based on direct ceramic machining, was invented. Since then the process and the materials were tested and introduced in the market as *Cercon*-Smart Ceramics. The strength and technology of Cercon allows bridges to be produced without metal substructure. Developments over the last ten years in ceramic materials science have led to a class of high strength materials such as alumina and zirconia based ceramics. Utilizing zirconia in the dental field opens the design and application limits of all-ceramic restorations. (1)

Zirconia is a white crystalline oxide of zirconium with the chemical formula ZrO_2. This ceramic material has a high flexural strength exceeding that of some types of steel and thus referring to as "steel" ceramic. Because of its hardnes, the material is used in situations subjected to high friction and wear. One of the most attractive features of zirconia is its high fracture toughness rendering the material less susceptible to crack propagation during function. The unique mechanical properties of zirconia allow its use as a core material for long span all-ceramic restorations with more confidence and success rate. Of interest to dentistry is the yttrium, partially stabilized, tetragonal zirconia, polycrystal material (Y-TZP). (2)

An attractive property of zirconium oxide ceramics is its high ***fracture toughness***. This is attributed to its crystalline transformation from tetragonal to monoclinic phase in response to mechanical stresses. Such transformation is associated with volumetric expansion, which is responsible for the generation of compressive fields intended to hinder a propagating crack tip. So this ceramics are said to be smart material forming a comprehensive solution with advantages of the esthetics, strength and fracture toughness. (2)

1. Smart Composite (containing amorphous calcium phosphate)

Amorphous calcium phosphate

Amorphous calcium phosphate (ACP) is one of the most soluble biologically important calcium phosphates, exhibiting the most rapid conversion to crystalline hydroxyapatite, which is an inorganic calcium-containing constituent of bone matrix and teeth, imparting rigidity to these structures. HAP. An old word which signifies to catch; as, "to hap the rent," to hap the deed poll.". It is the initial solid phase that precipitates from a highly supersaturated calcium phosphate solution, and can convert readily to stable crystalline phases such as apatitic products. Its morphological form, structural model and X-ray diffraction patterns are typical for noncrystalline substances with short-range periodic regularity. ACP has been demonstrated to have better in vivo osteoconductivity than hydroxyapatite, better biodegradability than tricalcium phosphate, good bioactivity (3).

Generally, it is believed that ACP was firstly described by Aaron S. Posner in the mid-1960s (4). It was obtained as an amorphous precipitate by accident when mixing high concentrations of calcium chloride and sodium acid phosphate in buffer (5). In X-ray diffraction, it was shown to have only two broad and diffuse peaks, with maximum at 25° 2θ. No other features were obvious, and it was clearly not apatite. This pattern is typical for substances that lack long range periodic regularity. It was found that immediately after being mixed, the spontaneously formed precipitate was a non-crystalline, or amorphous, calcium phosphate with calcium to phosphorus molar ratio (Ca/P) of 1.50. After several hours, it could convert to poorly crystalline apatite on ageing. Afterwards, this solid converts slowly to crystalline apatite (Ca/P = 1.67) by an autocatalytic mechanism (6).

ACP-filled polymeric composites

ACP could be incorporated as a filler phase in polymeric composites (7). Skrtic has developed unique biologically active restorative materials containing ACP as filler, which may stimulate the repair of tooth structure because of releasing significant amounts of calcium and phosphate ions. Thus, ACP incorporated into specially designed and formulated resins will act as a source for calcium and phosphate with extended time release nature. During a carious attack and the pH level in the mouth drops below 5.8, calcium and phosphate ions merge within seconds to form a gel. In less than 2 minutes, the gel becomes amorphous crystals, which transformed with time into the final apatite crystalline mineral and precipitates replacing the hydroxyapatite lost due to the acid attack.

Compared with more commonly used silanated glass or ceramic filler, more hydrophilic and biodegradable ACP-filled composites exhibited inferior mechanical properties, durability and water sorption characteristics. The uncontrolled aggregation of ACP particulates along with poor interfacial interaction plays a key role in adversely affecting their mechanical properties (8). Their clinical applicability may be compromised by relatively poor filler/matrix interfacial adhesion and also by excessive water sorption that occurs in both resin and filler phases of these composites (9, 10). However, trials are made to add silica or zirconia into ACP filler by introducing Si or Zr elements during low-temperature synthesis of the filler to improve the properties (3).

3-Smart Glass ionomer

Glass ionomer could be considered as a smart material owing to its inherent capability to react according to changes in the oral environment (11). It must be noted that ion migration within or through any material can occur in the presence of water. Since glass ionomer is ***water-based,*** it is not surprising that numerous studies have reported continuing release of fluoride from set glass ionomer over prolonged periods(12-14)and higher levels of fluoride release from glass ionomers as compared to other fluoride-containing restorative materials (15-17).

Glass ionomer materials can be said to be ***mimicking the behaviour of human dentine*** through a type of smart behaviour. The human dentine where very little dimensional change is observed on heating in wet conditions and a marked contraction is noted in dry conditions.(1) The smart behaviour of glass ionomers and related materials is closely linked to their water content and the way in which this can react to changes in the environment. Glass ionomers show little or no change in dimension when heated and cooled between 20°C and 50°C in wet conditions. (12, 13) In dry conditions the materials showed a marked contraction when heated above 50°C. The explanation for this behaviour is that in wet conditions, the fluid flow causes a balancing of the dimensional. In dry conditions, the rapid loss of water on heating results in the observed contraction.

In the case of Glass ionomers, the fluoride release rate can become negligible within a week (14). However; the smart behaviour of these materials offers some long term solutions to this problem. There is evidence that the fluoride released from salt phases can be replaced when the material is bathed in a high concentration of fluoride as may occur in a toothpaste or mouthrinse. In the long term, the fluoride rereleased after ***recharging*** may be much more important than the initial "burst "which is sustained only for a short time. The levels of fluoride release maintained can be increased by beginning the recharging process as soon as possible after setting. Various studies have shown that the rates of fluoride release and recharging are temperature sensitive. Hence, a more rapid recharging could be accomplished by using warm fluoride containing solutions and this can generate a more sustained release at mouth temperature (15).

There is gathering evidence that caries inhibition by glass ionomers not only is a question of *fluoride* release but also involves a continuing ***ion exchange*** among the restoration, the surrounding tooth structure, and the saliva. There is further evidence of the transfer of *calcium* and *phosphate* ions from tooth structure into the glass-ionomer restoration. (16, 17) The ion-exchange layer is more acid-resistant than both the glass ionomer and the enamel. It has been shown that the steady improvement in wear resistance results from movement of fluoride ions out of the restoration surface followed by the uptake of calcium and phosphate ions from the saliva to maintain the electrolytic balance in the restoration. (18)

In areas where high-risk children cannot afford dental care, a conservative holding technique has been advocated to seal remaining caries in a fluoride rich environment and establish some degree of remineralization. Atraumatic restorative treatments (ART) involve opening a lesion, removing soft surface decay, and filling or sealing the surface with high-filled glass ionomer with a fast setting time (11).

However, these products are known to have very limited durability and longevity due to their brittleness and solubility. Materials demonstrating an optimum combination of smart interactions and longevity are likely to have some combination of stable ***resin*** matrix combined with a co-existent salt matrix or discreet phase. Within the spectrum of materials which lie in the continuous scale between resin matrix composites and salt matrix glass ionomers, we are already able to identify various materials described as Resin Modified Glass Ionomer, Compomers or Giomers and these have been demonstrated as exhibiting some smart characteristics (19).

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Thermoresponsive Smart Polymers

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Abstract: Traditionally, materials designed for long term use in the body or more specifically in the mouth are thought to survive longer if they are 'passive' and have no interaction with their environment. Perhaps the first inclination that an 'active' rather than 'passive' material could be attractive was the realization of the benefit of fluoride release from materials..

Keywords: *Smart; restorative; Materials; polymer*

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Over the past few decades, materials had to meet increasing requirements. Reason for this is the continuous desire of mankind to raise the performance of all types of structures. To meet these increasing demands a large variety of high-performance materials have been used.

Traditionally, materials designed for long term use in the body or more specifically in the mouth are thought to survive longer if they are 'passive' and have no interaction with their environment. Perhaps the first inclination that an ***'active' rather than 'passive'*** material could be attractive was the realization of the benefit of fluoride release from materials (1).

Smart materials are a class of materials that are highly responsive and have the inherent capability to sense and react according to changes in the environment. For that reason they are often also called ***"responsive materials"***. The stimuli could originate internally or externally. Since its beginning, materials science has undergone a distinct evolution: from the use of passive materials to active materials, and finally to intelligent materials with more acute recognition, discrimination and reaction capabilities (2).

Thermoresponsive Polymers

One of the main groups of "smart" materials is based on polymers because they are cheaper and more easily tailored than metals or ceramics. These polymeric "smart" materials can respond to stimuli such as pH, temperature, chemical and biological stimuli. Polymers, respond to temperature, have biological related applications which include drug delivery, gene delivery and tissue engineering. Thermoresponsive polymers could be categorized based on their 3-dimensional structure; hydrogels, interpenetrating networks, micelles, crosslinked micelles, polymersomes and films (4).

1-a) Drug Delivery

Drug delivery, as the name suggests, is the method or process of administering a pharmaceutical compound (drug) to achieve a therapeutic effect in humans or animals. Key factors are to deliver the drug to the right area, at the right time and at the right concentration. However there are many obstacles to achieving successful drug delivery. To name a few, these obstacles include the drugs': low solubility, environmental or enzymatic degradation, fast clearance rates from the body, non-specific toxicity and inability to cross the biological barriers(5,6). In order to overcome these obstacles, drug delivery carriers are being used, most of which are based on polymers (5-7).

Nevertheless, even when using a carrier to deliver the drug it is difficult to have the desirable controlled release rate. Specifically, the delivery of a drug is often problematic because the concentration of the released drug at the target area is either too low or too high and is not delivered for the desirable amount of time. Thus, the desirable-controlled drug release that is often characteristic of a zero-order kinetic rate is not easily achievable. Consequently "smart" polymeric carriers are used to deliver drugs. These carriers allow delivery of the drug at the right time and concentration by only releasing the drug in response to an external stimulus. For example the polymer chains of a carrier may expand as a result of the temperature increasing, thus enabling the drug to diffuse out and be released from the carrier (8).

1-b) Gene Delivery

Gene therapy aims at the treatment of many genetic diseases as it is a technique for correcting defective genes that are responsible for these genetic diseases. Specifically, the delivery of the appropriate, therapeutic gene (DNA) into the cells that will replace, repair or regulate the defective gene that causes the disease is a vital step for gene therapy. DNA, however, is a negatively charged, hydrophilic molecule; thus its delivery into the nucleus of the cell which requires it to pass through the
also negatively charged and hydrophobic cell membrane is not feasible (4).

Consequently, gene delivery carriers (also called vectors or vehicles) have been developed (9, 10). Many of these are polymer-based because polymers are cheap, safe and also easier to tailor compared to other gene delivery carriers like liposomes (8-12). When using a polymeric carrier, also called transfection, involve the: (1) DNA and polymer complexation; (2) addition of DNA/polymer complex (sometimes also called polyplex) onto cells for a period of time commonly called the transfection time; (3) removal of complex from the cells; (4) incubation time that is when the cells are left to incubate for a time period until results are observed. Complexation is usually performed at room temperature whilst the incubation and transfection periods are at 37 °C (body temperature that the cells need to be in order to survive) (4).

1-c) Tissue Engineering

Tissue engineering as an interdisciplinary field that applies the principles of engineering and the life sciences towards the development of biological substitutes that restore or improve tissue function (13). The tissue engineering involves the use of a scaffold/material within which cells will be seeded and consequently tissue will mature. This requires the use of a biocompatible material/scaffold, usually natural materials like proteins or synthetic polymers, with the appropriate 3D structure that will provide sufficient mechanical support and has the ability to convey both nutrients and growth factors to encapsulated cells (14).

Thermoresponsive polymers in tissue engineering are commonly used in two situations: as substrates that enable the cell growth and proliferation and as injectable gels, for *in situ* of the scaffold. In the first application, the thermoresponsive ability of the polymers is used to regulate the cells' attachment and detachment from a surface. The second application involves the encapsulation of cells in a 3D structure in the body. The *in situ* formation of cell/scaffold contrast compared to the *in vitro* formation of the construct allows the delivery of encapsulated cells, nutrients and growth factors to defects of any shape using minimally invasive techniques. Specifically, the thermoresponsive polymer is mixed at room temperature with the cells and then injected into the body. Upon injection due to the temperature increase (to 37 °C), the polymer forms a physical gel. The cells are encapsulated within the 3D structure of the gel(4).

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