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REVIEW ARTICLE



# Orthodontic wires and its corrosion—The specific case of stainless steel and beta-titanium

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KEYWORDS corrosion; fluoride ions; orthodontic wires; pH Abstract Efficient orthodontic treatments rely on the perfect design and condition of orthodontic wires. Different wires made from different metals and alloys are available in the market. Although no wire is the best for the entire treatment, they must obey certain properties such as biocompatibility, formability, weldability, low coefficient of friction, resilience, shape memory, low stiffness, and high elastic limit. Even with the buildup of protective layers, wires exposed to the oral environment can suffer corrosion. This gradual destruction of materials resulting from chemical reactions can have several adverse effects such as the release of elements from metals, roughening of the wire surface, and weakening of appliances, which can lead to mechanical failure or even fracture of the orthodontic materials. Corrosion of orthodontic wires is strongly related with the acidic environment of the buccal cavity and the presence of fluoride ions, prophylactic agents, and mouthwash solutions. In this review, a brief description of the different commercially available wires is given. Moreover, the desirable features and properties to be considered in the search for the ideal wire are addressed. Finally, the role of pH and fluoride ions on the corrosion of wires is discussed. Results from different experiences over the years are likewise provided. Special attention is given to stainless steel and beta-titanium wires, because these two alloys are frequently used in the treatment phases in which the wires are exposed to the oral environment for lengthy periods. Copyright © 2014, Association for Dental Sciences of the Republic of China. Published by Else-

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# Introduction

Orthodontic treatment is vital for improving and maintaining good oral and dental health, as well as creating an attractive smile that contributes to the development of self-esteem.

The mechanical foundation of orthodontic therapy is based on the principle that stored elastic energy can be converted into mechanical work by tooth movement, and that the ideal control of tooth movement requires the application of a system of distinctive forces properly supported by accessories such as orthodontic wires.<sup>1</sup>

Model wires should be designed to move teeth with continuous forces and should remain elastic.<sup>2</sup> Different wire alloys are available for orthodontic treatment. However, no wire is optimal for orthodontic applications during all the different stages of treatment.<sup>2</sup> The properties required for orthodontic wires depend on their application, but commonly desirable mechanical characteristics include high springback, low stiffness, good formability, and low friction.<sup>3</sup> Nevertheless, several features and properties must be considered in the search for the ideal wire.

# Mechanical properties of orthodontic wires

In the past decades, a variety of wire alloys was introduced into orthodontics, leading to improvement of treatments. The appropriate use of the different existing wires may reduce the duration of the treatment and enhance patient comfort. Several characteristics of orthodontic wires are considered desirable for optimum performance during treatment. A brief description of each of these desirable wire characteristics is provided.

# Modulus of elasticity (stiffness)

Modulus of elasticity (stiffness) can be defined as the resistance to permanent deformation. It is proportional to the stiffness of the material<sup>4</sup> and can be determined by the binding forces between atoms. As these forces are constant for each metal structure, stiffness is a constant property of each metal. In orthodontics, it represents the force required to deflect or bend a wire.<sup>1</sup> Low stiffness wires are preferable because they provide the ability to apply lighter and more constant forces during arch deactivation.<sup>4</sup>

# Elastic limit

Elastic limit relates to the maximum amount of workload that can be applied to a wire before it undergoes permanent plastic deformation and can no longer return to its original shape. A high elastic limit, with low stiffness, is desirable.<sup>1</sup>

#### Resilience

Resilience is inversely proportional to the elastic limit and represents the amount of stored energy available in the wire to move teeth,<sup>4</sup> corresponding to the stored energy in the wire, when deformed elastically and released when unloaded. High levels of resilience are preferable.<sup>1</sup>

# Shape memory effect

Many materials will show a permanent deformation if their elastic limit is exceeded. However, after an apparent deformation, certain metals will return to their original shape when heated. This effect is called "shape memory effect". When materials return to their original form after reaching the point of deformation, the accumulated forces in the wire are dispersed in a consistent manner for a lengthy period, which is essential to assure teeth movement.<sup>1</sup>

# Formability, weldability, and friction

While weldability is the wire's ability to be fused to other materials, the formability of the wire is its ability to be bent into desirable shapes (such as loops and bends).<sup>1,2,4</sup> Friction refers to the resistance of a material when sliding over another and, in orthodontics, it corresponds to the quality of sliding between the wire and orthodontic accessories.<sup>4</sup>

# **Biocompatibility**

Because orthodontic wires are positioned close to the oral mucosa for lengthy periods, they should be resistant to corrosion and prevent the release of ions in the oral cavity, and should not cause allergic reactions. In other words, orthodontic wires must be biocompatible with oral tissues.<sup>1</sup>

# Different metals and alloys used in orthodontics

#### Stainless steel (FeCrNi; SS) alloys

Until the 1930s, the available orthodontic wires were made of gold. Austenitic SS was introduced as an orthodontic wire in 1929, and because of its superior strength, higher modulus of elasticity, good resistance to corrosion, and moderate costs, SS promptly gained acceptance and preference over gold.<sup>4</sup> The alloy of SS most frequently used for orthodontic materials is the American Iron and Steel Institute type 304, containing 18–20% of chromium and 8–10% of nickel.<sup>3,5</sup> SS wires have good biocompatibility, good corrosion resistance, excellent formability, high yield strength, and high modulus of elasticity.<sup>4,6</sup>

#### Cobalt-chromium (CoCr) alloys

Consisting of cobalt (40%), chromium (20%), silver (16%) and nickel (15%), this alloy was first developed in the 1940s for the manufacture of watch springs and found its place in orthodontics in the 1960s. Regardless of their greater resistance to fatigue and distortion, the mechanical properties of CoCr wires are very similar to those of SS.

#### Nickel-titanium alloys

Nickel-titanium (NiTi) alloys were introduced into clinical use in 1972. It was produced under the trade name Nitinol,

with a composition of 55% nickel and 45% of titanium. Several other brands of NiTi wires were launched in the market in 1976. However, none of these wires showed thermal activation, shape memory effect, or superelasticity. In 1985, a new superelastic NiTi alloy, developed especially for application in orthodontics, was reported.<sup>1</sup> NiTi alloys have good springback and flexibility that allow large elastic deflections.<sup>7</sup> Heat treatment of these alloys changes their crystallographic arrangement, producing the so-called "shape memory". This phenomenon results from a crystalline phase change known as "thermoelastic martensitic transformation" and describes the effect of restoring the original shape of a deformed wire by heating it through its transitional temperature range.<sup>8,9</sup> This transformation from the distorted to the original shape involves a transformation of nitinol from the martensitic to the austenitic phase. However, these alloys present poor formability, which is a disadvantage. Moreover, the bending of these wires has a harmful effect on their springback property.4

#### Copper-nickel-titanium alloys

Copper-nickel-titanium (CuNiTi) alloys consist of nickel, titanium, copper, and some chromium. These wires became available on the market in the mid-1990s. The addition of copper to the alloy enhances the thermal-reactive properties of the wire and makes it highly resistant to permanent deformation.<sup>1</sup>

#### Beta-titanium alloys

In 1979, Goldberg and Burstone<sup>6</sup> introduced for the first time a beta-titanium ( $\beta$ -Ti) alloy into orthodontic applications.  $\beta$ -Ti alloy is commercially available as "TMA" (titanium-molybdenum alloy) and, although one company owned its manufacturing rights for many years,<sup>10</sup> the alloy is currently marketed by a wide diversity of commercial brands.<sup>1</sup>  $\beta$ -Ti wires possess an excellent balance of properties suitable for many orthodontic applications such as good corrosion resistance, low potential for hypersensitivity, low stiffness, high springback, excellent formability, and good weldability, even compared with SS and cobalt-chromium-nickel orthodontic wires.<sup>3,6,10-12</sup> The modulus of elasticity of  $\beta$ -Ti is about twice that of nitinol and less than one-half that of SS, making it ideal for applications where less force than the one from steel is required, but where a lower modulus material such as nitinol would be insufficient to produce the desired force magnitude.<sup>4</sup> These properties allow a simplified appliance design that can deliver superior force without requiring the addition of loops and helices. In the beginning,  $\beta$ -Ti wires were used for specific applications in a segmented arch technique for the making of retraction loops. Nowadays,  $\beta$ -Ti are used in many applications such as intrusion arches, uprighting molar spring, and cantilevers for intrusion or extrusion of teeth.<sup>1</sup>

# Corrosion of orthodontic wires

Within orthodontics, nickel is one of the most commonly used metals in wires, as it is included in NiTi, SS, and other

alloys. However, nickel is the most common metal to cause contact dermatitis and to induce more cases of allergic reactions. Reports have suggested that a concentration of approximately 30 mg/L of nickel may be sufficient to prompt a cytotoxic response.<sup>13</sup> Moreover, some complexes of nickel have been considered carcinogenic, allergenic, and mutagenic.<sup>14</sup> NiTi allovs can have >50% of nickel content and, consequently, release sufficient nickel ions to cause allergic reactions.<sup>15</sup> Additionally, there have been reports of nickel-nonsensitive patients who have become nickel-sensitive after using NiTi wires.<sup>16</sup> SS has a nickel content of 8%, <sup>15</sup> but its crystal lattice binds the nickel ions, making them unavailable to react.<sup>13</sup> Hence, these low nickel content alloys are unlikely to cause nickel hypersensitivity, being tolerated by nickel-sensitive patients. Besides nickel, the suspected genotoxic chromium metal is also known to cause adverse biologic effects such as hypersensitivity, dermatitis, and asthma.<sup>17</sup>

Because of its ionic, thermal, microbiological, and enzymatic properties, the oral environment is favorable to the biodegradation of metal wires and their alloys, with consequent release of metal ions in the oral cavity.<sup>18</sup> The major process of degradation of metals is corrosion. Oral conditions such as the temperature, the quantity and acidity of saliva, the presence of certain enzymes, and the physical and chemical properties of solid and liquid food may influence corrosion processes.

Along with the release of elements from metals or alloys, corrosion of orthodontic wires can lead to roughening of the surface and weakening of the appliances and can severely affect the ultimate strength of the material, leading to mechanical failure or even fracture of the orthodontic materials.

To resist corrosion, SS, CoCr, and titanium alloys depend on the formation of a passive surface oxide film. However, even though these protective oxide films are present on the metal surface, metal ions can still be released.<sup>16</sup> Not only is the protective oxide layer susceptible to both mechanical and chemical disruption, but the oxide film can also slowly dissolve as the metal is exposed to oxygen from the surrounding medium. Acidic conditions and fluoride-containing products can contribute to these processes.<sup>19</sup> As a matter of fact, the corrosion and deterioration of certain metals and alloys have been related with the acidic environment of the buccal cavity and with the presence of fluoride ions in several toothpastes and mouthwash solutions.<sup>20–29</sup>

## Effect of pH in orthodontic wire corrosion

Metal corrosion is an electrochemical process in which a metal surface exposed to a conducting aqueous electrolyte usually becomes the site for two simultaneous chemical reactions: oxidation and reduction (redox). Taking iron in a weak acid solution as an example, the oxidation (or anodic reaction) results in the production of ferrous ions (Equation (1)), whereas reduction (or cathodic reaction) results in the consumption of electrons produced by the anodic reaction, with the production of hydroxide ions, water, or hydrogen gas (Equations (2)–(4)).

$$Fe_{(aq)} \rightarrow Fe_{(aq)}^{2+} + 2e_{(aq)}^{-}$$
<sup>(1)</sup>

$$O_{2(aq)} + 2H_2O_{(l)} + 4e^-_{(aq)} \rightarrow 4OH^-$$
 (2)

$$O_{2(aq)} + 4H^{+}_{(aq)} + 4e^{-}_{(aq)} \rightarrow 2H_2O_{(l)}$$
 (3)

$$2H_{(ag)}^{+} + 2e_{(ag)}^{-} \rightarrow H_{2(g)}$$

$$\tag{4}$$

Although the cathodic reaction represented by Equation (2) should be considered for corrosion processes under natural environments, under acidic (or even low acidic) environments Equation (3) and, particularly, Equation (4) are the most relevant, being the ones that should be taken into account regarding the corrosion of wires in the oral cavity.

The extension of corrosion will depend on the nature of the solvent in which the metal is immersed and, unless the metal can form a protective surface layer (passivation), the corrosion process endures until total consumption of the metal or the cathodic reactant occurs.

Metals in oral appliances are constantly challenged by acidic foods and liquids, such as soft drinks, which will supposedly promote the cathodic reaction of corrosion and, consequently, the anodic reaction (dissolution of the metal) as well.

The pH effect on orthodontic wires corrosion has been widely studied. In 2003, Huang et al.<sup>16</sup> measured the amount of ions released from NiTi wires immersed in artificial saliva with different pH values as a function of time. They concluded that the amount of released metal ions increased with immersion time in all conditions and that the amount was greater when more acidic solutions were involved. They also observed that the average amount of nickel ions released per day was higher in the first days, probably owing to the formation of a TiO<sub>2</sub> protective layer on the wire surface. This protective layer was confirmed through X-ray photoelectron spectroscopy (XPS) in 2004 by Huang,<sup>30</sup> who-resorting to cyclic potentiodynamic polarization curves and scanning electron microscopy (SEM)-also observed that the corrosion potential and corrosion rate increased with the decrease in pH value. Polarization curves can be very useful in the assessment of corrosion susceptibility, because they provide information on passivity, pitting susceptibility, and corrosion rate. Among others, Figueira et al.<sup>31</sup> used this technique to evaluate the susceptibility of NiTi commercial samples to corrosion resistance and the effect of pH on the corrosion behavior in solutions with different pH values. Although the increase in the pH value led to a decrease in the corrosion potential, no significant differences were detected in the passive behavior for the studied pH range, leading to the conclusion that NiTi has a good corrosion resistance. Moreover, in accordance with other studies, <sup>16,30</sup> their XPS studies reveal that, although the surface layer of NiTi after immersion in the different solutions has some  $Ni(OH)_2$  content,  $TiO_2$  is the main constituent.

# Effect of fluorinated and other prophylactic agents

Mouth rinsing with fluoride-containing products is an effective method for prevention of caries because of the

complicated morphologies of orthodontic appliances. Regular use of products containing fluoride during the course of orthodontic treatment is essential because fluoride ion can promote the formation of calcium fluoride globules that stimulate remineralization.  $^{32-34}$ 

Clinically available fluoride-containing products have a variety of fluoride concentrations (250–10,000 mg/L) and pH values (3.5–7).<sup>35,36</sup> Prophylactic fluoride gels with a low pH were found to be more effective in the increase of calcium fluoride (CaF<sub>2</sub>) formation.<sup>32</sup>

Reduction of corrosion resistance of pure titanium and titanium alloys in fluoride-containing environments has also been reported, <sup>37</sup> with the use of fluoride-containing rinses or gels being harmful to titanium in acidic environments. Titanium corrodes not only in the presence of sodium fluoride (NaF) in acidic solution but also at high pH values if the NaF concentration is considerably high.<sup>35</sup> The fluoride ions degrade the protective titanium oxide film formed on titanium and titanium alloys. The contact of electrolyte with the metal is possible through the pores of the oxide layer that can contain several oxides of different stoichiometries such as TiO, Ti<sub>2</sub>O<sub>3</sub>, or TiO<sub>2</sub>, although TiO<sub>2</sub> is the most frequently observed.<sup>38</sup>

Once titanium-based orthodontic wires become exposed to acidulated topical NaF products, hydrofluoric acid (HF) can be produced according to Equation (5), and HF will then rapidly dissolve titanium, in accordance with Equations (6) and (7), and/or 8, leading to corrosion of the metal alloy<sup>37,39</sup>:

$$H_3PO_4 + 3NaF \rightarrow Na_3PO_4 + 3HF$$
 (5)

$$Ti_2O_3 + 6HF \rightarrow 2TiF_4 + 3H_2O \tag{6}$$

$$IiO_2 + 4HF \rightarrow IiF_4 + 2H_2O \tag{7}$$

$$TiO_2 + 2HF \rightarrow TiF_2 + H_2O \tag{8}$$

In 2002, Schiff et al.<sup>36</sup> compared the electrochemical properties of different titanium alloys (TiAl<sub>6</sub>V<sub>4</sub>, NiTi, and NiTiCo, and pure titanium) according to the pH and fluoride content of the saliva. The polarization curve assays showed that for pure titanium and  $TiAl_6V_4$ , the corrosion rate increased as the medium became more acidic, then fluoridated and finally fluoridated-acidified. Although NiTi and NiTiCo were less affected by the fluoridated-acidified medium, fluoride had a negative effect on all materials. In agreement, surface analysis by SEM showed surface degradation on the tested alloys that had been exposed to fluoridated-acidified saliva. Later, in 2004, Schiff et al.<sup>34</sup> also assessed the corrosion influence of three commercial fluoride mouthwashes on four titanium alloys orthodontic wires (TMA, TiNb, NiTi, and CuNiTi). Corrosion potential was measured over time, and corrosion resistance of titanium alloys was determined. From the results obtained, it was possible to divide the alloys into two groups: one composed by nickel--titanium-based alloys (NiTi and CuNiTi), which were strongly corroded in the presence of monofluorophosphate found in one of the tested mouthwash solutions, and the other composed by TMA and TiNb, which were less resistant to corrosion in the presence of stannous and amine fluoride. These results were confirmed by SEM analysis of the alloys'

surface, emphasizing the need to recommend the proper mouthwash depending on the alloy used. In 2010, Lee et al.<sup>40</sup> evaluated the effect of fluoride prophylactic agents in four different brands of commercial NiTi archwires. The tests were made in acidic artificial saliva with different NaF concentrations (0.01%, 0.1%, 0.25%, and 0.5%), mimicking commercial fluoride-containing toothpastes. The polarization resistance of the different wires was calculated on the polarization curves experiments. Significant differences were found among the tested wires regardless of the NaF concentration in artificial saliva, although XPS analysis revealed a similar chemical composition of the passive film on the surface of all tested NiTi archwires. This apparent discrepancy could be due to different surface textures, roughness, and defects produced in the wires during the manufacturing process, which was observed by SEM and atomic force microscopy experiments. Nevertheless, all tested NiTi archwires revealed a decrease in corrosion resistance as the NaF concentration increased. This effect was more accentuated in high (0.5%) NaF-containing solution, which corresponds to a fluoride ion concentration of 2250 mg/L. These results are indicative of severe damage of the TiO<sub>2</sub>-based protective film and are in accordance with other previously reported studies showing that a fluoride ion concentration of 250–500 mg/L is enough to promote NiTi wire corrosion. 33,34

Corrosion of the TMA and NiTi alloys in fluorinated mouthwash solutions can also occur via hydrogen embrittlement.<sup>41,42</sup> This phenomenon can also be responsible for the degradation of the mechanical properties of titaniumbased alloys. In 2005, Walker et al.<sup>39</sup> evaluated the effects of different fluoride prophylactic agents on the mechanical properties of two nickel-titanium based NiTi orthodontic archwires (NiTi and CuNiTi) after being immersed in an acidulated fluoride agent and a neutral fluoride agent for 90 minutes at  $37^{\circ}$ C. Both unloading elastic modulus (E) and unloading yield strength (YS) had significantly decreased after fluoride exposure. However, the CuNiTi wire mechanical properties were not affected by fluoride agents. The variation in NiTi mechanical properties resulted from fluoride-related hydrogen embrittlement that affected the NiTi wire unloading-related phase shift. Regarding CuNiTi, the addition of copper appeared to have inhibited fluoriderelated degradation of the wire mechanical properties. Nevertheless, SEM assays for characterization of fluoride treatment effects on wires revealed that NiTi and CuNiTi wires suffered corrosive changes on surface topography.

# SS and beta-titanium

Usually, there are three phases in orthodontic treatments: 1 = leveling and aligning, 2 = space closure and anterior/ posterior correction, and 3 = detailing and finishing.  $\beta$ -Ti and SS wires are the most frequently used in Phases 2 and 3, which leaves them exposed to the oral environment for longer periods.<sup>43</sup> Thus, it is vital to understand their corrosion behavior. Both wires show high formability, which allows them to be bent into different configurations such as specialized loops.<sup>4,6</sup> Unlike titanium alloys, the passive layer of SS wires is composed of Cr<sub>2</sub>O<sub>3</sub>/Fe<sub>2</sub>O<sub>3</sub>.<sup>44,45</sup> Nevertheless, this corrosion resistance barrier can also be damaged. To determine the possible differences in the

corrosive potential of SS and TMA wires, Kim and Johnson<sup>46</sup> subjected these wires to anodic polarization in a physiologic solution (0.9% NaCl) with neutral pH. Results showed that TMA wires exhibited the lower corrosive potential. In addition, SEM photographs revealed that SS wires were readily susceptible to corrosion. Similar results were observed by Huang,<sup>44</sup> who-after conducting cyclic potentiodynamic and SEM analysis of SS wires in acid artificial saliva at 37°C-detected that the pH had a significant influence on the corrosion parameters of the stressed SS wires. In 2006, Lin et al.<sup>45</sup> performed SEM, atomic force microscopy, and linear polarization analysis and showed that SS wires from different brands and types, with different surface roughness and defects, presented significant differences in their corrosion resistance. Although only pH seems to be harmful to SS wires,<sup>47</sup> both pH and fluoride concentration have negative effects on  $\beta$ -Ti wires, with hydrogen embrittlement in fluoride solutions being one of the reasons for  $\beta$ -Ti alloy fracture during clinical treatment.<sup>10</sup> Nevertheless,  $\beta$ -Ti corrosion resistance behavior is higher than that in other wires.<sup>48</sup> In 2003, Watanabe and Watanabe<sup>49</sup> assessed surface roughness and colors after immersion of TMA wires in fluoride prophylactic agents with different pH values and observed that the TMA immersed in acidic fluoride solution changed color and surface morphology within 1 hour, exhibiting a high surface roughness after 24 hours. This is in accordance with other studies<sup>50-52</sup> showing that degradation of mechanical properties in  $\beta$ -Ti orthodontic wires increases with longer immersion periods. In 2007, Walker at al<sup>43</sup> evaluated the effect of fluoride prophylactic agents on the loading and unloading elastic modulus and yield strength of  $\beta$ -Ti and SS wires. After the wires were immersed for 90 minutes in different fluoride solutions at 37°C, the functional unloading mechanical properties of both wires decreased in acidulated and neutral fluoride agents. Moreover, SEM experiments showed corrosive changes on the surface topography of both wires after exposure to both solutions.

### **Concluding remarks**

Over the years, there have been great concerns about the impact of orthodontic wire corrosion. The literature suggests that metal ions are released during orthodontic treatment, but the level is far lower than that ingested in a routine daily diet. The effects of pH and fluoride concentration on  $\beta$ -Ti and SS wires might be negative in prolonged orthodontic treatment time. It is a proven fact that corrosion of orthodontic treatment and on patient's health is still not fully understood. Future work in more clinically relevant conditions is vital for better comprehension. It would be interesting to conduct additional assays and test the effect of other properties on corrosion, such as fatigue resistance when subjected to force applied to the wires.

## **Conflicts of interest**

The authors have no conflicts of interest relevant to this article.

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