Corrosion resistance of stainless steel, nickel-titanium, titanium molybdenum alloy, and ion-implanted titanium molybdenum alloy archwires in acidic fluoride-containing artificial saliva: An *in vitro* study

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**ABSTRACT**

**Objective:** (1) To evaluate the corrosion resistance of four different orthodontic archwires and to determine the effect of 0.5% NaF (simulating high fluoride-containing toothpaste of about 2250 ppm) on corrosion resistance of these archwires. (2) To assess whether surface roughness (Ra) is the primary factor influencing the corrosion resistance of these archwires. **Materials and Methods:** Four different archwires [stainless steel (SS), nickel-titanium (NiTi), titanium molybdenum alloy (TMA), and ion-implanted TMA] were considered for this study. Surface characteristics were analyzed using scanning electron microscopy, atomic force microscopy (AFM), and energy dispersive spectroscopy. Linear polarization test, a fast electrochemical technique, was used to evaluate the corrosion resistance, in terms of polarization resistance of four different archwires in artificial saliva with NaF concentrations of 0% and 0.5%. Statistical analysis was performed by one-way analysis of variance. **Results:** The potentiostatic study reveals that the corrosion resistance of low-friction TMA (L-TMA) > TMA > NiTi > SS. AFM analysis showed the surface Ra of TMA > NiTi > L-TMA > SS. This indicates that the chemical composition of the wire is the primary influential factor to have high corrosion resistance and surface Ra is only secondary. The corrosion resistance of all wires had reduced significantly in 0.5% acidic fluoride-containing artificial saliva due to formation of fluoride complex compound. **Conclusion:** The presence of 0.5% NaF in artificial saliva was detrimental to the corrosion resistance of the orthodontic archwires. Therefore, complete removal of residual high-fluorinated toothpastes from the crevice between archwire and bracket during tooth brushing is mandatory.

**KEY WORDS:** Corrosion resistance, fluoride, polarization resistance

Orthodontic wires are formed into various configurations or appliances to apply forces to teeth and move them into desirable alignment. Various types of metallic orthodontic wires are used in the treatment of malocclusion based on their properties.

In the oral environment, orthodontic attachments are exposed to a number of potentially damaging physical and chemical agents. Corrosion, the graded degradation of materials by electrochemical attack, is of concern particularly when orthodontic appliances are placed in the hostile electrolytic environment provided by human mouth. Electrolytic or electrochemical corrosion occurs in the oral cavity due, in part, to the wet environment. The surface of certain metals reacts with oxygen to form a surface oxide layer, which inhibits an...
attacking substance from reaching the metal surface. Corrosion of a metal that is covered by a protective film is dependent upon the properties of the film. Metallic materials are not susceptible to corrosion as long as the surface oxide layer is intact but when the breakdown potential of an alloy is reached, the oxide layer dissolves and the onset of surface corrosion and pitting begins. Pitting corrosion is the most common type of corrosion seen in orthodontic wires and brackets because they are not perfectly smooth. At a microscopic level, they can exhibit many pits. This feature is thought to increase the susceptibility to corrosion because of their ability to harbor plaque forming microorganisms. These microorganisms cause localized reduction in pH and depletion of oxygen, which in turn affect the passivation process.

The clinical significance of corrosion includes (1) corrosion increases orthodontic friction force between the archwire/bracket interface due to increase in surface roughness (Ra); (2) corrosion products have been implicated in causing local pain or swelling in the region of orthodontic appliances in the absence of infection, which can lead to secondary infection; (3) Cytotoxic and biological responses; and (4) Weakening of appliance. Acids and chloride ions can accelerate corrosion process. Therefore, a diet rich in sodium chloride and acidic carbonated drinks provides a regular supply of corrosion agents. Another contribution to acidic oral conditions is fluoride-containing products. In dental applications, fluoride-containing, commercial mouthwashes, toothpastes, and prophylactic gels are generally used to avoid dental caries or to reduce dental sensitivity. The fluoride ions can exhibit many pits. This feature is thought to increase the susceptibility to corrosion because of their ability to harbor plaque forming microorganisms. These microorganisms cause localized reduction in pH and depletion of oxygen, which in turn affect the passivation process.

The purpose of this study is to determine the corrosion resistance of various orthodontic wire alloys and to determine the effect of fluoride (0.5% NaF), simulating commercial fluoride-containing toothpastes, and prophylactic gels are generally used to avoid dental caries or to reduce dental sensitivity. The fluoride ions can exhibit many pits. This feature is thought to increase the susceptibility to corrosion because of their ability to harbor plaque forming microorganisms. These microorganisms cause localized reduction in pH and depletion of oxygen, which in turn affect the passivation process.

Materials and Methods

Commercial archwires of stainless steel (SS), nickel-titanium (NiTi), titanium molybdenum alloy (TMA), and low-friction TMA (L-TMA) were used (0.017 × 0.025 Ormco, Glendora, California, USA).

Scanning electron microscope (Hitachi, SU6600, Japan) was used to observe the surface morphology of the archwires. Elemental composition of the archwires was assessed using energy dispersive spectroscopy (EDS) (Horiba-Emax). Atomic force microscope (AFM) (XE-100 Park, Korea) was used to evaluate the three-dimensional surface Ra of the archwires.

A potentiostat (Gill AC, ACM Instruments, England) was used to perform the linear polarization test, a fast and nearly nondestructive electrochemical technique. Archwires samples cut into 40 mm were used as working electrode. A saturated calomel electrode and platinum were used as the reference electrode and counter electrode, respectively. Modified Fusayama artificial saliva (NaCl [400 mg/L], KCl [400/mg/L], CaCl₂ H₂O [795 mg/L], NaH₂ PO₄ H₂O [690MG/L], KSCN [300 mg/L], Na₂ S 9H₂O [5 mg/L], and Urea [1000 mg/L]) with a pH of 6.5 at 37°C was used as the corrosion test electrolyte. To evaluate the effect of fluoride concentration on these archwires, 0.5% of NaF (simulating the fluoride concentration contained in commercial fluoridated toothpastes) was added to modified Fusayama artificial saliva.

Experimental groups

Eight groups were taken, and the sample size was 10 for each of these groups. The experimental groups are mentioned below:

- Group 1: SS in artificial saliva
- Group 2: NiTi in artificial saliva
- Group 3: TMA in artificial saliva
- Group 4: L-TMA in artificial saliva
- Group 5: SS in artificial saliva with 0.5% NaF
- Group 6: NiTi in artificial saliva with 0.5% NaF
- Group 7: TMA in artificial saliva with 0.5% NaF
- Group 8: L-TMA in artificial saliva with 0.5% NaF

The linear polarization tests were carried out after dipping the archwire samples into the test electrolyte for 2 h. The linear polarization values were measured from −10 mV to +10 mV with a scan rate of 0.1 mV/S. From the present test, the polarization resistance (R_p [Ω cm²]) was obtained which is inversely proportional to the corrosion rate and directly proportional to corrosion resistance.

Results

Figure 1 shows the SEM observations of the different archwires. Figure 2 and Table 1 show the AFM observations and the corresponding surface (Ra, nm). TMA wires showed the greatest surface Ra. This was followed by NiTi, L-TMA, and SS, respectively. Statistical analysis using one-way analysis of
Table 1: Surface roughness (Ra, nm) for different wires

|     | SS   | NiTi | TMA | L-TMA |
|-----|------|------|-----|-------|
| Ra  | 43.96(4.71) | 79.66 (9.84) | 124.00 (30.04) | 73.46 (13.36) |

Table 2: Polarization resistances (Ω cm²) for various groups in artificial saliva without sodium fluoride

|     | SS without NaF | NiTi without NaF | TMA without NaF | L-TMA without NaF |
|-----|----------------|------------------|-----------------|-------------------|
| Rp  | 46.042.80      | 91,576.60        | 278,439.20      | 279,229.40        |
|     | (2241.47)      | (3459.60)        | (8636.26)       | (8731.56)         |

Table 3: Polarization resistances (Ω cm²) for various groups in artificial saliva with sodium fluoride

|     | SS with NaF | NiTi with NaF | TMA with NaF | L-TMA with NaF |
|-----|-------------|---------------|--------------|----------------|
| Rp  | 724.10      | 2081.60       | 7118.20      | 7225.80        |
|     | (146.41)    | (447.96)      | (1183.87)    | (1405.32)      |

Figure 2: Atomic force microscopic images. NiTi: Nickel titanium, TMA: Titanium molybdenum, L-TMA: Low-friction titanium molybdenum alloy

Discussion

The SS and titanium alloys used in orthodontic appliances rely on the formation of a passive surface oxide film to resist corrosion. The protective layer is not infallible; it is susceptible to both mechanical and chemical disruption. Potentiodynamic polarization experiments and scanning electron microscopic observations of archwires composed of SS, NiTi, and TMA exposed to electrochemical corrosion in artificial saliva have shown evidence of pitting corrosion formed on the wire surface.

As for SS archwires, it is well known that chromium element in the SS alloy can form a thin and adherent Cr₂O₃-based protective film which provides the corrosion resistance of a substrate alloy. A minimum chromium content of around 11% is required to form a protective passive film on the SS wire.[10] In case of NiTi archwires, the TiO₂-based (also small traces of NiO) passive film can provide a good measure of NiTi alloy biocompatibility.[11,12] TMA wires form a passive film of TiO₂ and traces of MoO₃, ZrO₂, SnO, and L-TMA form the same protective layer as TMA wire together with the formation of traces of NO due to ion bombardment of nitrogen.[13] Edie et al.[14] in their study stated that the corrosion potential of SS and NiTi is not different. However, the present study [Table 3] suggests that more surface pitting and corrosion occurred in SS than in NiTi, TMA, and L-TMA. These results were almost similar to the results reported by Suarez et al. and Kim and Johnson.[12,15] They concluded that the titanium wires appear to be the most inert wire of those tested and are unlikely to release metal ions when used intraorally. They also stated that nitride coating did not affect the corrosion of the alloy. However, in this study, L-TMA was found to have a slightly higher corrosion resistance than TMA wires. This result was consistent to the results obtained earlier.[16] Ion implantation decreased friction and improved the corrosion resistance decreasing the corrosion rate. The improvement in corrosion resistance of L-TMA was believed due to the presence of NO in the outermost surface of the alloys.[11] It was found that TiO₂-based passive film formed on titanium metal has better corrosion resistance in acidic artificial saliva than the Cr₂O₃-based passive film on SS. This result was also consistent with a previous study which has also concluded that TiO₂ passive film is more corrosion resistant than Cr₂O₃.[10] The better corrosion resistance of TMA wires than NiTi might be due to the increased titanium content in them (78% in TMA and 45% in NiTi).[11] This is clearly seen in the present study in which the composition of the archwire is determined by energy dispersive spectroscopy (EDS).

A previous study[17] had suggested that surface Ra of orthodontic archwires ought to be taken as an important indicator of the trend toward archwire corrosion resistance. In our study [Table 1], TMA showed the highest surface Ra value and SS the least surface Ra. From the potentiostatic tests, it was confirmed that TMA and L-TMA exhibited the highest corrosion resistance. Contrary to this, earlier studies were reported[7,18] but our study was consistent with the study reported by D’Anto et al.[19] From this, it can be concluded that chemical composition of the wire is the primary factor influencing the corrosion resistance and surface Ra is only secondary.
From Table 3, it is very clear that the corrosion resistance of all wires had reduced drastically in the presence of 0.5% NaF (although L-TMA showed the highest RP value). The Cr₂O₃ passive film of SS reacts with NaF and the following reaction takes place:

\[
\text{Cr}_2\text{O}_3 + 2\text{NaF} \rightarrow \text{CrF}_2 + \text{Na}_2\text{O} + \text{CrO}_2
\]

In case of NiTi and TMA wires, TiO₂ reacts with NaF to form titanium-fluoride complex compound.[10,21]

\[
\text{TiO}_2 + \text{NaF} \rightarrow \text{Na}_2\text{TiF}_6
\]

However, TMA and L-TMA archwires showed a better corrosion resistance than NiTi. This may be due to the presence of some other oxides in the surfaces passive film (MOO₃, ZrO, ZrO, and SnO). [13]

**Conclusion**

From the AFM analysis, TMA showed the highest surface Ra. This was followed by NiTi, L-TMA, and SS in decreasing order. From the potentiostatic study, it was found that TMA and L-TMA had the highest corrosion resistance. This indicates that the chemical composition of the wire is the primary influential factor to have high corrosion resistance and surface Ra is only secondary.

In the present study, the RP values were measured after exposing the archwires to artificial saliva and artificial saliva-containing sodium fluoride (0.5%) for 2 h. This simulated the in vivo corrosion resistance of the archwires in the oral cavity. It also simulated the in vivo corrosion resistance of archwires when residual fluorinated toothpastes interacted with the archwires 2 h after brushing. It was seen that the in vivo corrosion resistance of the archwires in the oral environment might decrease if the highly fluorinated toothpastes were used and/or the exposure time of archwires to residual fluorinated toothpastes was prolonged. Therefore, complete removal of residual high-fluorinated toothpastes from the crevice between archwire and bracket during tooth brushing is required. Furthermore, the repair of the protective surface oxide film on the archwires might occur after full removal of residual fluorinated toothpastes by mechanical tooth brushing.

However, the effect of a lesser concentration of fluoride and variation in the exposure time to this particular concentration of fluoride on the archwires is still to be investigated.

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**Conflicts of interest**

There are no conflicts of interest.

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