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EFFECTS OF FLUORIDE ON CORROSION PROPERTIES OF ORTHODONTIC
RETENTION WIRES

By

John J. Simindinger, DDS

A Thesis submitted to the Faculty of the Graduate School,
Marquette University,
in Partial Fulfillment of the Requirements for
the Degree of Master of Science

Milwaukee, Wisconsin

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ABSTRACT
EFFECTS OF FLUORIDE ON CORROSION PROPERTIES OF ORTHODONTIC
RETENTION WIRES

John J. Simindinger, DDS

Marquette University, 2021

Objective: Alloys used in retention wires corrode in the oral environment. Previous studies have examined the effects of fluoride on archwires used in active treatment, but not on retention wires. The goal of this study was to determine what effect fluoride exposure has on corrosion of various lingual bonded retainer wires in the mouth.

Methods: Twenty samples from six different wire types were tested in two solutions. Half were tested in Fusayama-Meyer artificial saliva, while the other half were tested in Fusayama-Meyer plus fluoride correlated to the concentration of toothpaste. A potentiostat was used to measure open circuit potential (OCP) for three hours, polarization resistance (R_p), and corrosion current (I_{corr}). A potentiodynamic curve was produced which revealed if pitting corrosion occurred in each wire.

Results: In general, the OCP at three hours and R_p of the wires were significantly ($p < 0.05$) greater in artificial saliva than artificial saliva plus fluoride. I_{corr} was significantly greater in the fluoride-containing artificial saliva. The solid stainless steel displayed the greatest OCP at three hours and the highest R_p of any wire in both solutions. The gold plated twisted had a significantly greater I_{corr} than any other wire in artificial saliva. Stainless steel twisted had the second highest value, which was also significantly greater than the remaining four wires. However, when fluoride was added the stainless steel twisted had the greatest I_{corr} , followed by gold plated twisted. Both of these wires had significantly greater I_{corr} values than the other wires in the fluoride containing solution. Gold plated solid had the lowest I_{corr} in this solution and was the only wire whose I_{corr} did not increase when fluoride was added. Pitting corrosion was present in the stainless steel twisted wire in both solutions and in both gold plated wires in artificial saliva.

Conclusion: Twisted wires experience significantly greater corrosion rates than solid wires of the same composition. Conformation and composition are important in corrosion susceptibility. Gold plating increases a wire's R_p and may lower its I_{corr} , reducing its susceptibility to corrosion in the presence of fluoride. Fluoride increases the susceptibility of most wires to corrosion.

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CHAPTER 1 INTRODUCTION

Following active orthodontic treatment, long term retention is necessary. Gingival tissues, periodontal ligament fibers, and alveolar bone must reorganize and adapt to the final location of the teeth. Relapse of teeth towards their original location or in the direction of unbalanced forces is likely without some form of retention helping to hold them in place until this reorganization takes place (Pratt et al., 2011). While the collagenous fibers within the gingiva normally complete their reorganization within four to six months, the elastic supracrestal fibers are still capable of displacing a tooth more than a year after the cessation of active orthodontic treatment (Proffit et al., 2019). This is especially true for teeth that were heavily rotated or badly displaced at the start of treatment.

One of the most impactful factors influencing relapse is the continued growth of the jaws following orthodontic treatment. Patients who will experience growth following removal of orthodontic appliances will need to continue retention at least until growth has slowed to adult levels. This is especially true for patients whose initial malocclusions were related to their skeletal growth pattern. In general, growth will continue in the original pattern even after treatment, which puts these patients at risk for recurrence of the same types of malocclusion (Proffit et al., 2019). Studies on the cephalocaudal gradient of growth have demonstrated that the maxilla and mandible follow differing growth curves, with the mandible growing longer and later into life than the maxilla. Late mandibular growth results in increased mandibular incisor irregularity in individuals whether they have had orthodontic treatment or not (Driscoll-Guilland, et al., 2001).

While facial growth is one contributor to the need for retention, even adult patients with minimal facial growth remaining experience posttreatment crowding as a result of other factors. Arch expansion is a common aspect of orthodontic treatment and instability related to it contributes to relapse potential. Studies have shown greater stability of expansion in the absence of extractions with the posterior region being where expansion techniques are most effective. Studies have also shown posterior expansion to be more readily achieved when anteroposterior movement of the arches takes place as well. A maxillary arch that is being moved distally is capable of expansion and can accommodate expansion of the mandibular arch. In general, stable expansion of the mandibular intercanine width is unlikely unless the canines are lingually displaced by occlusion prior to expansion (Lee, 1999). Development of interproximal caries and subsequent restorations have been shown to increase posttreatment malalignment as well. This is often due to restorations not matching the tooth's original size and shape. Additional factors affecting posttreatment relapse include sex, ethnicity, missing teeth, and circumferential supracrestal fibrotomy procedures (Myser et al., 2013).

Regardless of which factors are promoting relapse in each individual case, it is clear that retention is vital to the long term stability of orthodontic results. Changes to the body with age are inevitable and this includes structures of the oral cavity and dentition. Even in healthy individuals, dentitional adjustments and changing dental relationships are unavoidable. Thus, the only way to maintain long term stability is through long term retention (Nanda & Nanda, 1992). To achieve this long term stability, clinicians commonly utilize fixed retainers bonded to the lingual surface of the teeth most likely to relapse or experience malalignment. Fixed retainers remain in place indefinitely and are subjected to

the physical and chemical insults of the oral environment. The objective of this study was to determine the effects of fluoride specifically on the corrosion properties of several commonly used fixed lingual retainer wires in the oral environment.

CHAPTER 2 LITERATURE REVIEW

Fixed retainers

A fixed retainer is a segment of wire bonded to the lingual surface of two or more teeth in order to prevent these teeth from relapsing back to their pretreatment positions. Common locations for fixed retainers are the lingual surfaces of the four maxillary incisors and from mandibular canine to canine. In the mandible, some clinicians prefer to bond all six anterior teeth to the wire, whereas others choose to bond the canines only. Fixed retainers are useful for preventing diastemas from reopening and for maintaining alignment of teeth that were originally rotated or crowded. They can also be used posteriorly to hold extraction spaces closed, but this is less common. In these cases, the wire would be bonded to the buccal surface of the teeth adjacent to the extraction space (Graber et al., 2017). Anterior lingually bonded retainers have the benefit of being hidden from view. Many patients consider posterior buccally bonded retainers to be minimally visible and esthetically acceptable as well (Axelsson & Zachrisson, 1992). Patients and orthodontists alike may prefer fixed retainers because they function without the need for patient compliance. Removable retainers only work if a patient commits to wearing and maintaining them appropriately. In contrast, fixed retainers commonly remain in place for years or even decades without issue. One study found 98.9% of mandibular and 97.6% of maxillary fixed retainers were still in place 10 to 15 years after placement (Kocher et al., 2019). Another study found that bonded retainers were more effective at maintaining mandibular incisor alignment in the first six months after debonding of braces than vacuum formed retainers (O'Rourke et al., 2016). However, it should be noted that numerous

retainer types and retention plans are considered effective. Provider preference plays a role in deciding what each patient is prescribed.

A common criticism of fixed retainers is that they collect plaque and make it difficult to maintain good oral hygiene. However, Eroglu et al. found no difference in periodontal status between patients with fixed and removable retainers. This included plaque index, gingival index, bleeding on probing, and probing depths (Eroglu et al., 2019).

Fixed retainers frequently come in either a thick 0.030-0.032 inch wire or a multistranded 0.0195-0.0215 inch twist wire. Thick solid wires are generally used in the mandibular arch and often bonded solely to the canines. However, these wires can be bonded to incisors as well if the provider deems it necessary. Twist wires are used in both arches and normally bonded to every tooth that they contact. Some practitioners may prefer to use 5-stranded over 3-stranded twist wires due to a tendency of the 3-stranded wires to unravel and introduce torquing forces on teeth in certain circumstances. Fixed retainer wires also differ in their composition. There are many commercially available variations including stainless steel, cobalt-chromium alloys, beta-titanium alloys, and more. Wires with protective gold coatings can be found as well.

A key quality that practitioners must keep in mind when choosing a fixed retainer wire is its relative stiffness. An ideal wire is stiff enough to prevent teeth from moving toward relapse, yet elastic enough to permit the physiologic movements that teeth experience during function (Zachrisson, 2015). Factors related to wire stiffness include conformation, distance between points of adhesion, diameter, and composition. A solid wire has greater stiffness than a multistranded wire of the same diameter (Graber et al.,

2017). It is also true that for wires of the same diameter, a shorter length of wire is stiffer than a longer length. Thus, for a fixed retainer of a given length, stiffness increases as the wire is bonded to more teeth. If the stiffness is too great and individual teeth in a segment are unable to move slightly and independently, bond failures between the teeth or the wire and the composite resin frequently occur (Zachrisson, 2015). Because solid wires are stiffer than multistrand wires, they require a longer span between points of adhesion in order to allow for physiologic tooth movements. This is why solid wires are commonly bonded to the canines only. The more flexible nature of multistrand wires necessitates that they be bonded to the incisors as well as the canines in order to gain enough stiffness to prevent relapse.

As there is currently no universal consensus among practitioners on wire type and bonding protocol, orthodontists are free to develop their own fixed retainer preferences. However, factors such as effectiveness at maintaining incisor alignment, rate of debonding and wire breakage, and ease of oral hygiene should be considered when choosing between solid and multistranded wires. According to Al-Nimri et al., multistranded wires are significantly more effective at maintaining incisor alignment than solid wires (Al-Nimri et al., 2009). Renkema et al. reported greater than 90% success rate of maintaining perfect mandibular anterior alignment five years posttreatment when using multistrand twist wires bonded to incisors and canines (Renkema et al., 2011). Most of the relapse observed in this study was due to bonding failures. Kocher et al. echoed this result in their study, which also found the most common reason for failure of fixed retainers to be composite damage and detachments (Kocher et al., 2019). However, the use of solid wires helps avoid this problem as they detach from teeth less frequently and experience fewer fractures than

multistranded wires (Störmann & Ehmer, 2002; Al-Nimri et al., 2009). As far as oral hygiene is concerned, the type of fixed retainer used does not affect the amount of plaque accumulation. Accumulation increases for teeth in contact with the fixed retainer regardless of type (Störmann & Ehmer, 2002). Additional factors that contribute to a practitioner's choice of fixed retainer protocol include individual clinical experience, material costs, and patient sensitivities.

Corrosion of orthodontic alloys

In the first half of the 20th century, orthodontists relied upon using precious metal alloys for orthodontic purposes. While pure gold is too soft to be useful, alloys containing platinum, palladium, copper, and gold were used effectively. However, with the introduction of stainless steel in 1929, precious metals were largely phased out of use for both functional and economic reasons. Today, stainless steel and some cobalt-chromium alloys have better strength, springiness, and equivalent corrosion resistance to precious metals (Proffit et al., 2019).

The most common stainless steel formulation is called type 304 and contains 18-20% chromium and 8-10% nickel (Castro et al., 2015). The relatively high chromium content is responsible for stainless steel's rust resistance, while the nickel helps maintain the austenitic phase of stainless steel (Kusy, 1997). Chromium causes rust resistance by reacting with oxygen in the environment to create a passive surface layer. Formation of this non-reactive passive layer is key because the corrosion process will continue until the metal or cathodic reactant is totally consumed if such a layer is not formed (Castro et al., 2015).

Following the introduction of stainless steel, a cobalt chromium alloy known as Elgiloy was developed. Made up of 40% cobalt, 20% chromium, 16% iron, 15% nickel, and other elements, Elgiloy shared many of stainless steel's properties. These included similar stiffness, with greater formability. As time went on, beta-phase titanium alloys were also developed, containing 80% titanium, 11.5% molybdenum, 6% zirconium, and 4.5% tin (Kusy, 1997). These wires exhibited even lower corrosive potential than their predecessors (Castro et al., 2015).

Corrosion is an electrochemical process that results in the loss of essential metallic properties of a metal. It occurs either through loss of metal ions directly into solution or by progressive dissolution of a surface film, typically an oxide or sulfide, on the metal. The corrosion process consists of two reactions – oxidation at the anode and reduction at the cathode. The anodic reaction dissolves metal atoms, displacing them into the surrounding environment as ions. Saliva within the oral cavity contains a complex mixture of dissolved electrolytes and enzymes. Although saliva acts as a buffer, foods and drinks can still create an acidic oral environment. Such an electrolyte-rich, acidic environment predisposes metal alloys to corrosion (Fraunhofer, 1997).

As mentioned above, a passive oxide layer on the surface of orthodontic alloys protects them from corrosion. However, these passive layers can dissolve under certain conditions, leaving the underlying metal exposed and vulnerable. It is possible for passive layers to reform, but failure to do so may allow the anodic reaction to significantly degrade the exposed metal. In the absence of a passive layer, noble metals such as gold are the most stable and resistant. Many studies have shown that orthodontic alloys readily corrode in the oral environment, including stainless steel (Castro et al., 2015; Kim et al., 1999). When

stainless steel wires corrode, significant amounts of chromium, nickel, and iron ions leach out of the wire and can be detected (Kuhta et al., 2009). On the other hand, Kim et al. found very little corrosion of beta-titanium alloy under these conditions (Kim et al., 1999). One factor that can impact the presence of a passive layer is the presence of fluoride. Fluoride has been shown to predispose alloys to pitting corrosion by combining with hydrogen ions in acidic environments to form hydrofluoric acid (HF) which both dissolves the passive layer and prevents it from reforming (Barcelos et al., 2013; Fraunhofer, 1997). This is especially relevant because pitting corrosion is considered even more destructive than a uniform corrosive attack (Castro et al., 2015). Whereas pitting corrosion occurs across the surface of a metal, crevice corrosion is a phenomenon that occurs when a nonmetallic material comes into contact with a metal. In the junction between the metal and non-metal, an oxygen depleted environment forms, which prevents the passive layer from reforming. Thus, resulting in increased corrosion (Eliades & Athanasiou, 2002). Practitioners must be aware that such crevice corrosion may occur anywhere bonding material is applied to a fixed retainer wire to attach it to a tooth.

Corrosion of metals in the oral environment is of clinical importance for two main reasons. First, corrosion of wires leads to a decay of their mechanical properties. Prolonged corrosion results in roughening of a wire's surface and inherent weakening of the metal, which can ultimately lead to mechanical failure of the appliance (Castro et al., 2015). Such failures become even more likely in the presence of both corrosion and repeated mechanical loading of the appliance. (Fraunhofer, 1997). Therefore, minimizing corrosion is essential for ensuring appliance longevity, especially for appliances intended to function in the mouth for 10 years or more. The second clinical concern related to corrosion of

metals in orthodontic appliances is the potential for deleterious biological effects on the patient.

Biocompatibility

The term biocompatibility can be summarized as the ability of a material to perform its desired function with respect to a medical therapy without eliciting any clinically significant adverse effects in the host (Schmalz, 2014). This concept may clash with the process of corrosion, which results in the release of metallic ions into the oral cavity that may affect the surrounding tissues. This is especially relevant and potentially concerning to the field of orthodontics, which employs a number of different metals and alloys in the makeup of appliances. Many studies have examined the biocompatibility of orthodontic archwires, bands, and brackets. These appliances are present in the mouth for two to three years on average, a relatively short time span in comparison to fixed retainer wires which are commonly in place for decades. Despite this discrepancy in duration of time spent in the mouth, few studies have been published examining the biocompatibility of fixed retainer wires.

The biocompatibility of an alloy in the oral cavity is dependent upon the metals that make it up and the level of corrosion it experiences. Researchers are able to determine the effects of metal ions released during corrosion on biologic systems by measuring either cytotoxicity or genotoxicity. While cytotoxicity measures the level of cellular damage, genotoxicity examines the presence of DNA damage in the form of chromosomal breakage or gene mutation. Nickel and chromium ions have been linked to these negative biological effects (Martin-Cameán et al., 2015). A European council

directive has gone so far as to classify nickel and chromium as toxic substances and suggest restricting nickel exposure of the skin to $0.5 \mu\text{gcm}^{-2}\text{week}^{-1}$ (Milheiro et al., 2012; Mikulewicz et al., 2012). Studies quantifying the release of nickel and chromium ions from orthodontic wires generally find the levels to be below that required to cause a toxic systemic effect but high enough to elicit an allergic reaction (Milheiro et al., 2012; Kuhta et al., 2009). In fact, nickel is the most common metal to cause contact dermatitis and to induce allergic reactions. Some complexes of nickel have even been considered carcinogenic, allergenic, and mutagenic (Castro et al., 2015). Anecdotal evidence supporting these findings can be found in case reports detailing allergic reactions caused by orthodontic appliances (Feilzer et al., 2008). Aġaoġlu et al. published a study examining nickel and chromium levels in saliva and serum of patients with fixed orthodontic appliances up to two years after appliance insertion. They recorded statistically significant serum increases in ion concentration in patients two years post insertion. Nickel and chromium levels were found to be highest in saliva in the first month with fluctuating levels during different time periods of treatment. Ultimately, the authors concluded that although nickel and chromium levels did not reach toxic levels in the serum or saliva, measurable amounts of these metals were released with unknown long term consequences (Aġaoġlu et al., 2001).

The effects of metal ions on the tissues of the oral cavity have been explored in several studies. Gursoy et al. investigated the role of nickel in orthodontic treatment induced gingival hyperplasia and found an increase in epithelial thickness and a significant increase in epithelial cell proliferation in response to low-dose nickel concentrations, with a toxic response to a higher dose. The authors concluded it is

plausible that continuing low-dose nickel release to epithelium could be the initiating factor of the gingival overgrowth that occurs during orthodontic treatment (Gursoy et al., 2007). Another study found that oxidative imbalance induced by nickel might induce apoptosis of oral epithelium cells (Trombetta et al., 2005). The juxtaposition of findings between these studies highlights the complexity of nickel induced sequelae for cells of the oral cavity. An in vitro study performed by Rose et al. examined the influence of corrosion products from several orthodontic archwires on a fibroblast culture. In their study, stainless steel and beta-titanium wires had no effect on the rate of cell proliferation. However, Elgiloy caused growth inhibition of the fibroblast cells, which was related to the concentration of corrosive cobalt and nickel ions in the eluate. The researchers also examined the corrosion rate of each alloy utilizing coupled plasma atomic emission spectroscopy, which found corrosion rate to be positively correlated with the level of cytotoxicity (Rose et al., 1998).

The potential toxicologic effects of nickel and cobalt on cells of the oral cavity seen in in vitro studies are corroborated in in vivo studies as well. Faccioni et al. found these metals to be present in greater concentrations in cells harvested from patients undergoing treatment than in cells from control subjects. Researchers also confirmed that these metals can produce DNA breaks in cells of the oral mucosa and noted a larger number of apoptotic cells in patients with fixed appliances (Faccioni et al., 2003). In a separate study by Fernández-Miñano et al., buccal mucosal epithelium was collected from patients wearing stainless steel, nickel-free, or titanium brackets. Cells in contact with the stainless steel and nickel-free brackets experienced DNA damage, while no

genotoxicity was seen in the cells surrounding titanium brackets (Fernández-Miñano et al., 2011).

Although corrosion products of orthodontic alloys have been shown not to reach toxic systemic levels, studies have demonstrated that biological effects are induced in patients by such corrosion products. Considering the frequent utilization of fixed retainers and their relatively long lifespan, there is a lack of available research pertaining to them specifically. The effects of fluoride on archwires and brackets have been studied numerous times. However, the effects of fluoride on fixed retainer wires of different compositions have not yet been determined. The objective of this study was to clarify what effect fluoride exposure might have on corrosion of fixed retainer wires in the oral cavity.

Fluoride

Community water fluoridation began in the United States in 1945. Studies have demonstrated a reduction in caries in both the deciduous and permanent dentition as a result (Iheozor-Ejiofor et al., 2015). Fluoride works in multiple ways to prevent dental caries. This includes promoting remineralization of incipient lesions, increasing enamel resistance to acid demineralization, interfering in the formation and functioning of dental plaque micro-organisms, and by increasing the rate of post-eruptive maturation. When pH levels in the mouth rise in the presence of fluoride, new and larger fluoride crystals containing fluorhydroxyapatite form, which reduce enamel demineralization and enhance remineralization. Fluoride containing dental products commonly use several different fluoride formulations. The most common are sodium fluoride (NaF), sodium mono-

fluorophosphate, stannous fluoride, and acidulated phosphate fluoride (APF). Fluoride dentifrices are considered the most effective agents for preventing enamel demineralization and they typically contain 1,000 ppm fluoride, though variations with 5,000 ppm are available and may be more suitable for patients with high caries risk (Mittal et al., 2017). Due to the nearly ubiquitous nature of fluoride in dental products, orthodontists should assume that any retention device prescribed for a patient will be exposed to fluoride and its effects.

Several studies have examined the effects of fluoride exposure on wires used for active orthodontic treatment. Močnik et al. found that increasing fluoride concentrations do not affect the properties of stainless steel 304 alloy. They noted that dental archwires made from this material were susceptible to local corrosion when exposed to lower fluoride concentrations, whereas at the highest concentrations a passive layer formed preventing local corrosion (Močnik et al., 2017). In contrast, Heravi et al. found that the corrosion resistance of archwires diminished with increasing sodium fluoride concentration up to 0.2% weight, possibly due to the destructive effect of fluoride on the protective oxide coating. The corrosion current increased with elevated sodium fluoride levels in their study as well (Heravi et al., 2015). The conflicting findings of these two studies illustrate the need for further research into fluoride's effects on orthodontic alloys used in active treatment as well as retention.

CHAPTER 3 MATERIALS AND METHODS

In this study, six types of metal fixed retention wires were selected and tested. Two wires were made up of stainless steel: Nubryte from Dentsply GAC (Bohemia, NY), a 0.028-inch solid wire; and Tri-Flex Twisted Wire from Rocky Mountain Orthodontics (Denver, CO), a 0.0215-inch 3-stranded wire. Another Rocky Mountain Orthodontics product, a 0.028-inch solid wire made up of Blue Elgiloy – a cobalt chromium alloy - was tested as well. Additionally, two gold-plated stainless-steel wires from Gold'n Braces (Palm Harbor, FL) – Penta Twist, a 0.0215-inch 5-stranded wire and a 0.028-inch solid wire – were used. Lastly, Retainium, a 0.028-inch beta-titanium ribbon from Reliance Orthodontic Products was tested. The diameters of both the solid and multistranded wires included in this study were selected because they match fixed retainer wires commonly used in practice. Retainium is only available in the size 0.028-inch ribbon used here. However, similar products are available in differing diameters for the other wires tested. The table below details the compositions of the wires tested.

Table 1. Compositions of the tested wires, by weight

<u>Wire</u>	Iron	Chromium	Nickel	Cobalt	Manganese	Aluminum	Titanium
Stainless Steel - Solid	69.8	18.6	8.8	0.2	1.3	-	-
Stainless Steel - Twisted	65-75	15-20	8-12	0-5	0-2	0-2	-
Gold Plated** - Solid	67.8-75	17-19	8-10	-	0-2	-	-
Gold Plated** - Twisted	67.8-75	17-19	8-10	-	0-2	-	-
CoCr	16	20	15	40	2	-	-
Beta-Titanium	0-5	0-10	0-0.9	-	-	0-40	50-100

* Compositions are as reported by the manufacturer/vendor

**Compositions of the gold plated wires are of the underlying wire. Both wires are plated with 23+ karat gold with cobalt added

Twenty segments of each of the six wire types were randomly assigned to one of two groups corresponding to the test solutions used ($n = 10$ per group, per wire). Each wire was cut into a five inch segment, of which 25 mm was isolated using nail lacquer. For gold plated wires, the isolated segment was at the end of the wire to ensure the sample was completely coated in the gold plating. Each wire was tested only a single time.

Each of the wire types was first tested in Fusayama-Meyer artificial saliva solution containing 0.4 g/L each of potassium chloride and sodium chloride, 0.6 g/L of calcium chloride, 0.69 g/L of sodium phosphate monobasic dihydrate, and 1 g/L of urea. This first test was done to determine the general corrosion of each type of fixed retainer wire. Once the first half of the wires had been tested using this solution, a new solution was produced containing the same ingredients plus 0.2% sodium fluoride. By isolating the presence of fluoride as the only altered variable, its affects were able to be studied.

An electrochemical cell set up was utilized to run each test. A reference electrode (saturated calomel electrode or SCE), a graphite rod acting as the counter electrode, and the wire to be tested were placed in a lidded beaker through holes in the lid. Enough artificial saliva, with or without the addition of fluoride, was added to the cell to fully submerge the isolated segment of the wire. The wire being tested as well as the other electrodes were connected to leads, or alligator clips, coupled to a potentiostat (Gamry PC4; Warminster, PA).

First, the open circuit potential (OCP), measured in mV, was recorded for three hours. Next, polarization resistance was measured by scanning potential from -20 mV (vs. OCP) to +20 mV at a scan rate of 0.1mV/s while measuring the resultant current.

Polarization resistance (R_p) in $M\Omega$ was calculated using Ohm's law ($R_p=V/I$) by measuring the slope of the line when voltage was plotted versus current. Lastly, a potentiodynamic curve was created by cycling potential between -300 mV and +700 mV (vs. OCP) at 1 mV/s while measuring current. Corrosion current (I_{corr}), measured in nA, could then be calculated using the Gamry software. The direction of each curve revealed if pitting corrosion had occurred. OCP at three hours, R_p , and I_{corr} were recorded for all tests. Because each of the wires had different diameters and surface areas based on their conformation, corrosion current was measured for each 25 mm length segment of wire and not normalized for surface area. Determining the surface area of the twisted wires would have been especially difficult and this was not considered practical. Therefore, the current measured is representative of the amount of current flowing from a wire with a length commonly used intraorally for retention, rather than a normalized area in contact with solution.

Data gathered for OCP at three hours, R_p , and I_{corr} was compared between wire types as well as between the two solutions – with and without Fluoride. The data was also further examined using a two-way analysis of variance (ANOVA), with type of wire and solution as factors. A post hoc analysis with a Tukey test was performed as well.

CHAPTER 4

RESULTS

Each of the six wire types were tested as described above. Table 2 displays the mean values for open circuit potential (OCP), polarization resistance (R_p), and corrosion current (I_{corr}) for the tests using artificial saliva and artificial saliva plus fluoride solutions. Two-way ANOVA showed significant ($p < 0.05$) differences with respect to wire and solution, as well as a significant ($p < 0.05$) interaction between them. Generally, the open circuit potential at three hours and polarization resistance of the wires were significantly ($p < 0.05$) greater in artificial saliva compared with the fluoride-containing artificial saliva. The opposite was observed with corrosion current; I_{corr} was significantly ($p < 0.05$) greater in the fluoride-containing artificial saliva. Due to the significant interaction between wire and solution, one-way ANOVA was used to compare wires within solutions and the rankings are denoted in Table 2 via letters (A, B, etc.) to denote mean values that are not significantly different within the table ($p > 0.05$). Multiple letters are used to indicate cases in which the mean values overlap with two significantly different categories. An A corresponds to the mean value that experiences the least corrosion in each measurement.

As illustrated in Table 2, the solid stainless steel wire displayed the greatest OCP at three hours in both solutions. Therefore, it can be considered the most noble wire. This wire also exhibited the greatest polarization resistance in both solutions, significantly greater than all other wires. In artificial saliva, cobalt chromium had the lowest OCP at three hours, slightly lower than stainless steel twisted. However, in the artificial saliva plus fluoride solution, beta-titanium's OCP at three hours was the lowest, with stainless steel twisted once again second lowest. The two twisted wires (stainless steel and gold plated)

had the lowest polarization resistances in the artificial saliva, with the gold plated wire having the lowest. These two wires had similarly low values when fluoride was added to the artificial saliva. In the fluoride containing solution, stainless steel twisted had the lowest R_p , while gold plated twisted and beta-titanium tied for second lowest. In general, the polarization resistance values were lower in the fluoride containing solution than in the artificial saliva alone. This value dropped for four of the six wires once fluoride was added and in the two remaining wires (gold plated twisted and gold plated solid) the values were nearly the same in both solutions. The same could be said for OCP at three hours. Once again four of the six values dropped once fluoride was added, with only gold plated twisted and cobalt chromium exhibiting greater nobility when fluoride was present.

Table 2. Electrochemical properties of the retainer wires

Wire	Artificial Saliva			Fluoride		
	OCP (mV vs. SCE) @ 3 hours	R_p (M Ω)	I _{corr} (nA)	OCP (mV vs. SCE) @ 3 hours	R_p (M Ω)	I _{corr} (nA)
Stainless Steel - Solid	216 ± 12 A	19.1 ± 4.4 A	23.6 ± 6.4 A	140 ± 55 A	13.3 ± 5.5 A	33.2 ± 8.5 A
Stainless Steel - Twisted	-43 ± 69 C	3.2 ± 2.4 DE	154.2 ± 110.3 B	-133 ± 31 D	0.4 ± 0.3 C	392.2 ± 170.4 B
Gold Plated - Solid	174 ± 81 A	7.7 ± 1.4 C	16.6 ± 7.2 A	67 ± 18 B	8.7 ± 2.3 B	6.6 ± 3.2 A
Gold Plated - Twisted	82 ± 43 B	0.6 ± 0.2 E	341.3 ± 123.8 C	116 ± 32 AB	0.7 ± 0.3 C	388.2 ± 241.7 B
CoCr	-44 ± 14 C	5.4 ± 1.1 CD	45.3 ± 14.0 A	-18 ± 16 C	3.1 ± 0.7 C	58.4 ± 11.7 A
Beta-Titanium	29 ± 40 B	14.0 ± 2.6 B	8.3 ± 1.5 A	-228 ± 61 E	0.7 ± 0.3 C	56.9 ± 23.2 A

The gold plated twisted wire had a significantly greater corrosion current (I_{corr}) than any of the other wires in artificial saliva. Stainless steel twisted had the second highest value, which was also significantly greater than the remaining four wires. Beta-titanium had the lowest I_{corr} in artificial saliva. However, when fluoride was added the stainless steel twisted wire had the greatest I_{corr} , followed closely by gold plated twisted. Both of these twisted wires had significantly greater I_{corr} values than the other wires. Gold plated solid had the lowest I_{corr} in this solution and was the only wire whose corrosion current did not increase when fluoride was added to the artificial saliva.

Figures 1-2 show the OCP of each type of wire in artificial saliva and fluoride solution, respectively. The OCP is measured as no current is flowing through the wire and is a general measure of the wire's susceptibility to corrosion. Lower values indicate that a wire is more likely to corrode, whereas greater values indicate greater corrosion resistance.

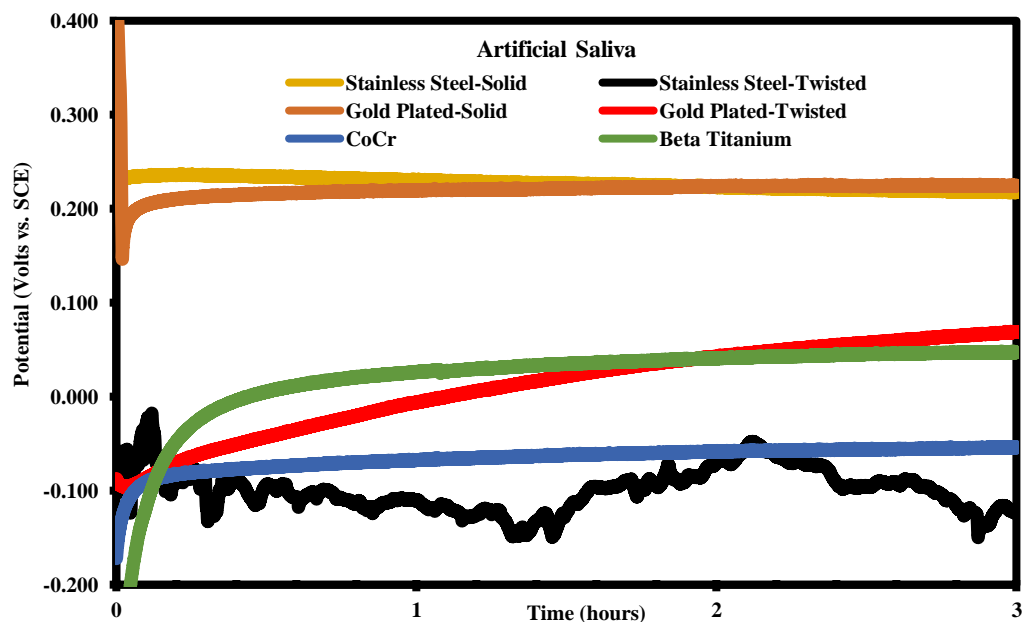


Figure 1. OCP of all wires in artificial saliva from 0-3 hours

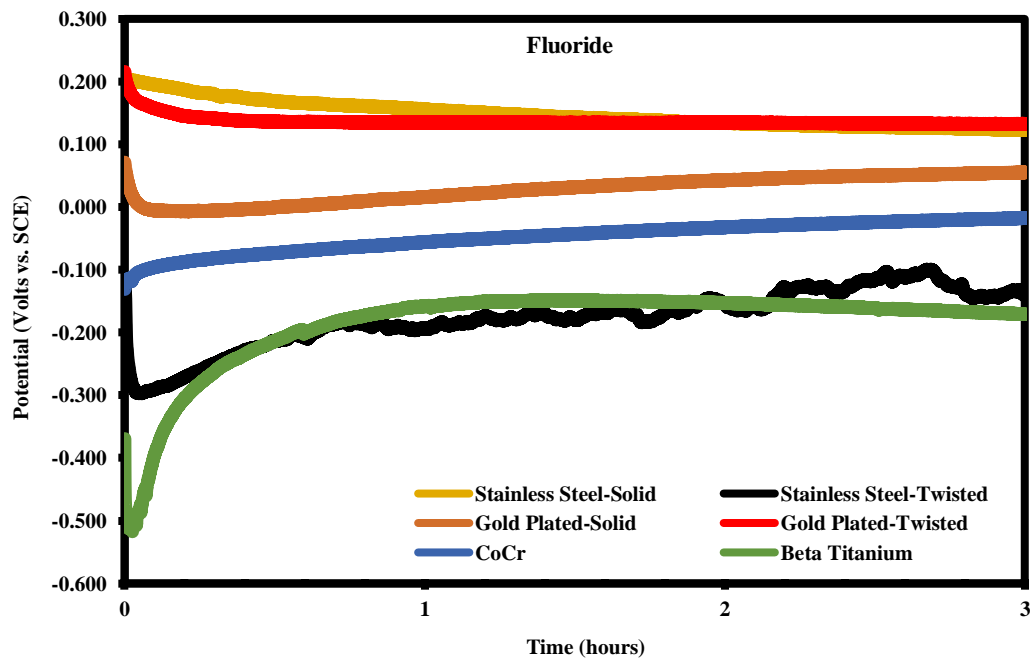


Figure 2. OCP of all wires in fluoride solution from 0-3 hours

Figures 3-4 illustrate the polarization resistance of each type of wire in artificial saliva and fluoride solution, respectively. Polarization resistance is equal to the slope of the lines plotted in figures 3 and 4. A line with a lower slope, or more horizontal line, indicates that a wire composed of that material is more susceptible to corrosion.

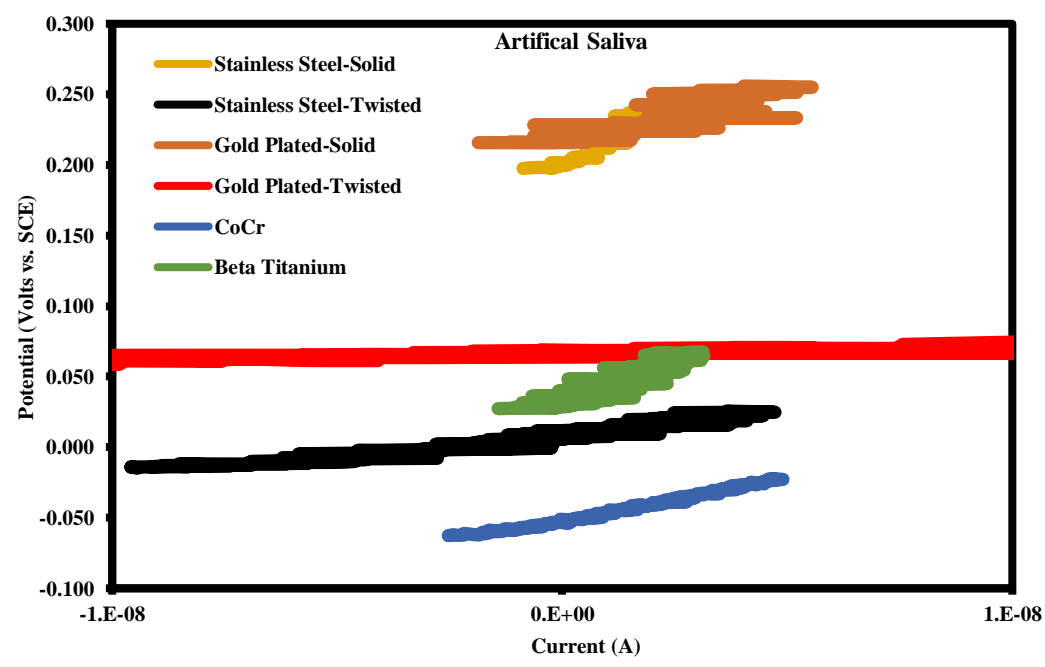


Figure 3. Polarization resistance of all wires in artificial saliva

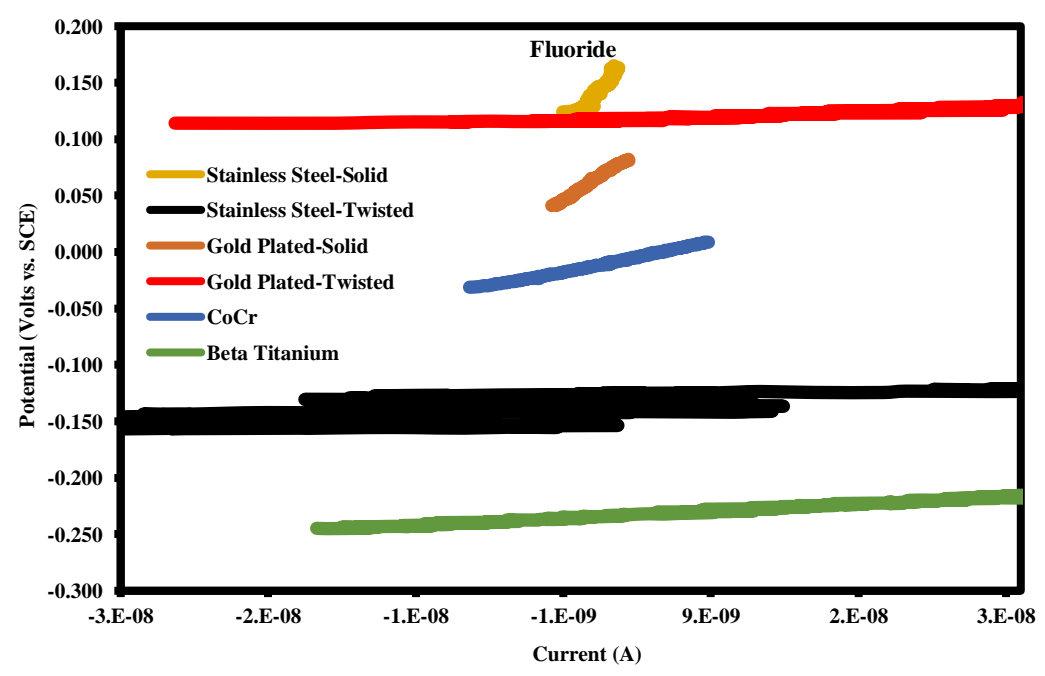


Figure 4. Polarization resistance of all wires in fluoride solution

Figures 5-10 show the potentiodynamic curves representing each individual wire type in artificial saliva. Potentiodynamic curves are a graphical display of each wire type's corrosion behavior. A curve that descends to the right from its peak indicates that pitting corrosion took place, while a break to the left indicates that it did not.

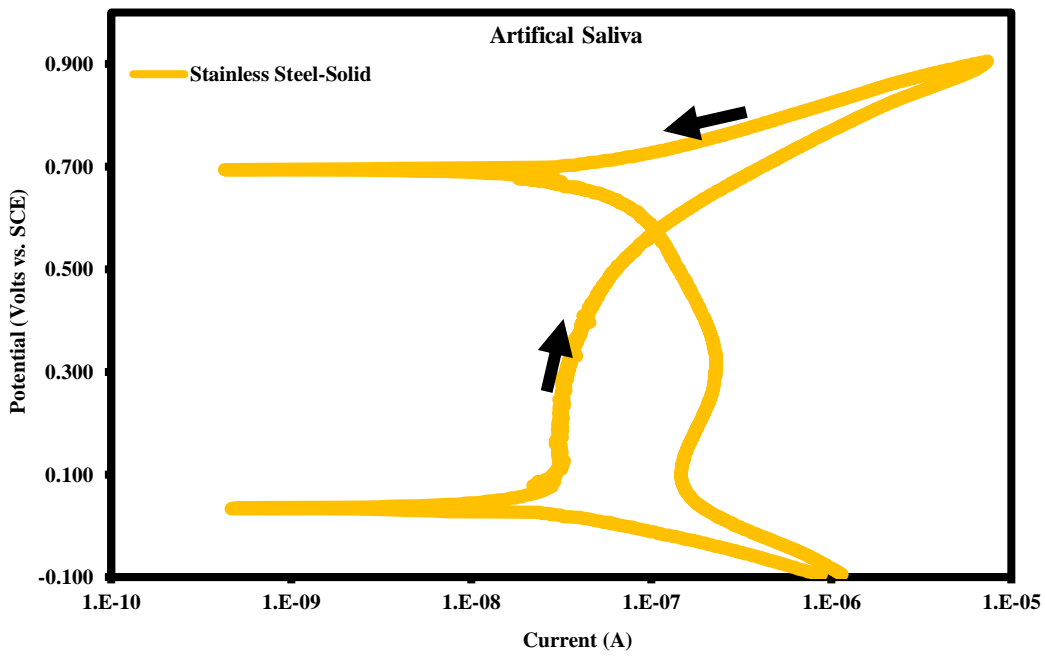


Figure 5. Potentiodynamic curve of solid stainless steel wire in artificial saliva

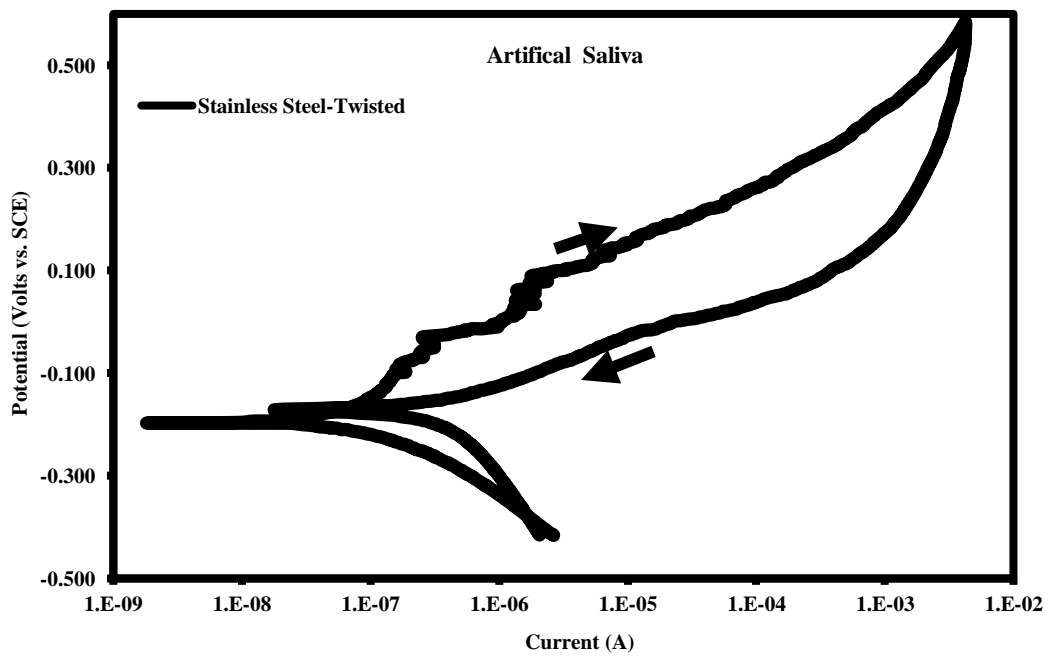


Figure 6. Potentiodynamic curve of twisted stainless steel wire in artificial saliva

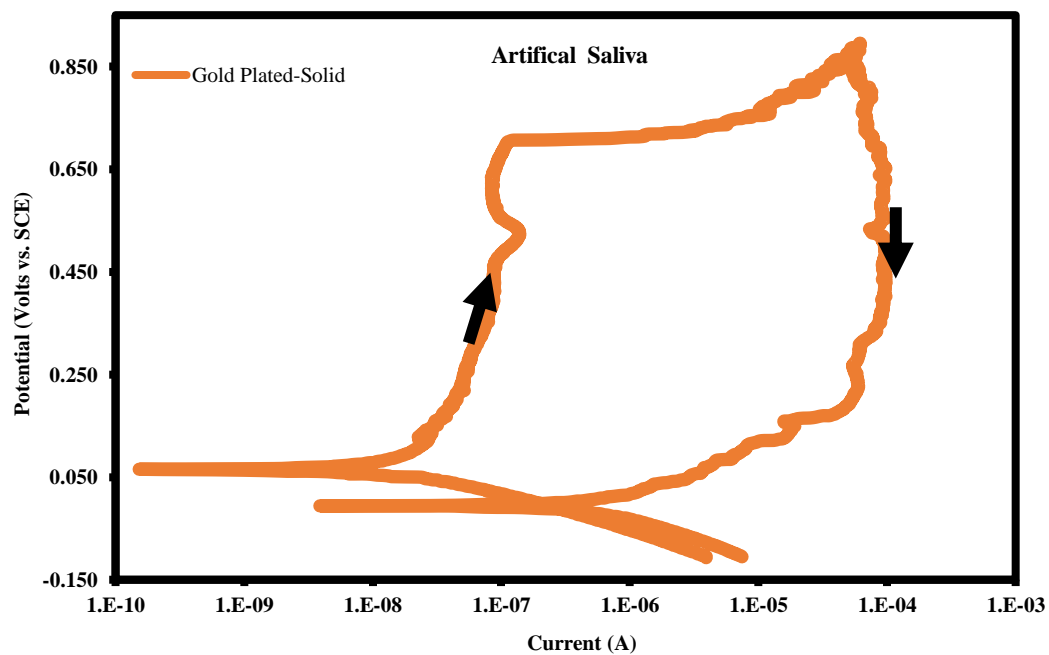


Figure 7. Potentiodynamic curve of solid gold plated wire in artificial saliva

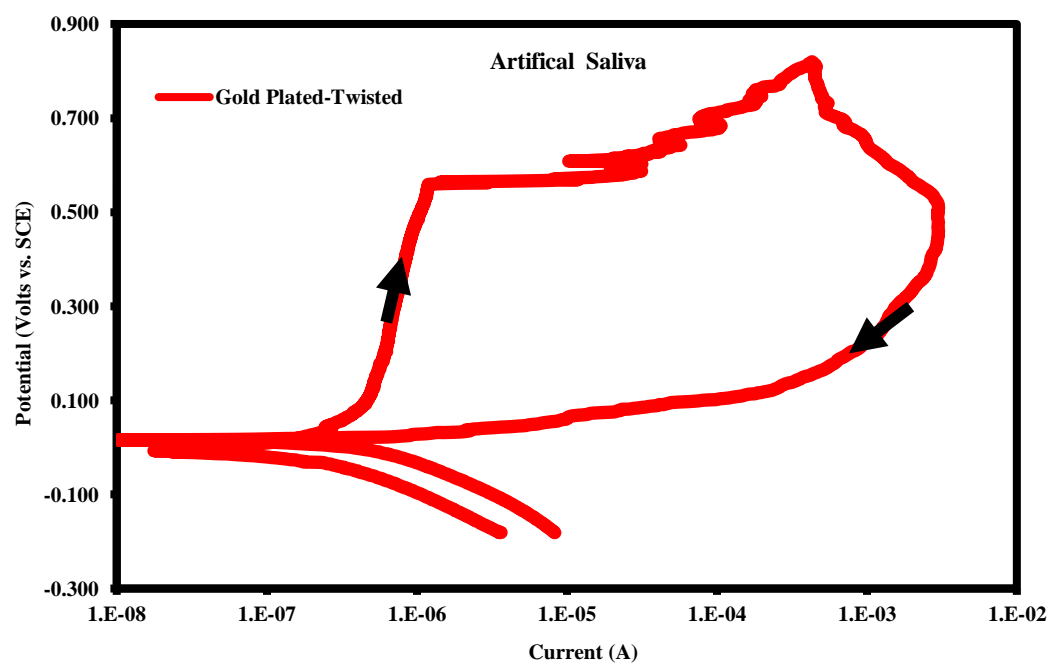


Figure 8. Potentiodynamic curve of twisted gold plated wire in artificial saliva

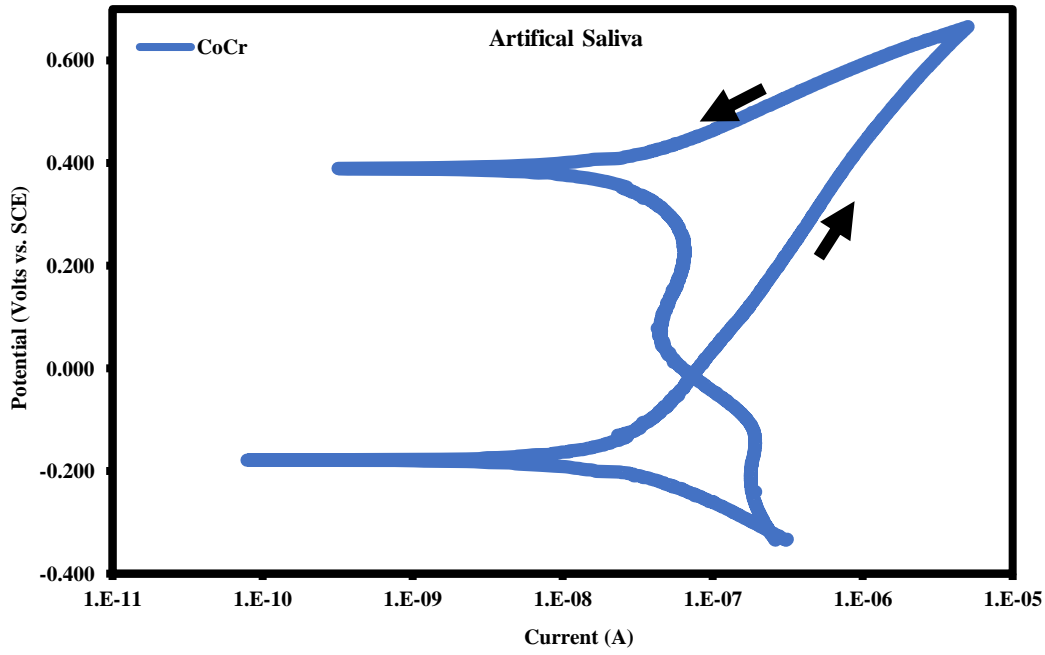


Figure 9. Potentiodynamic curve of cobalt-chromium wire in artificial saliva

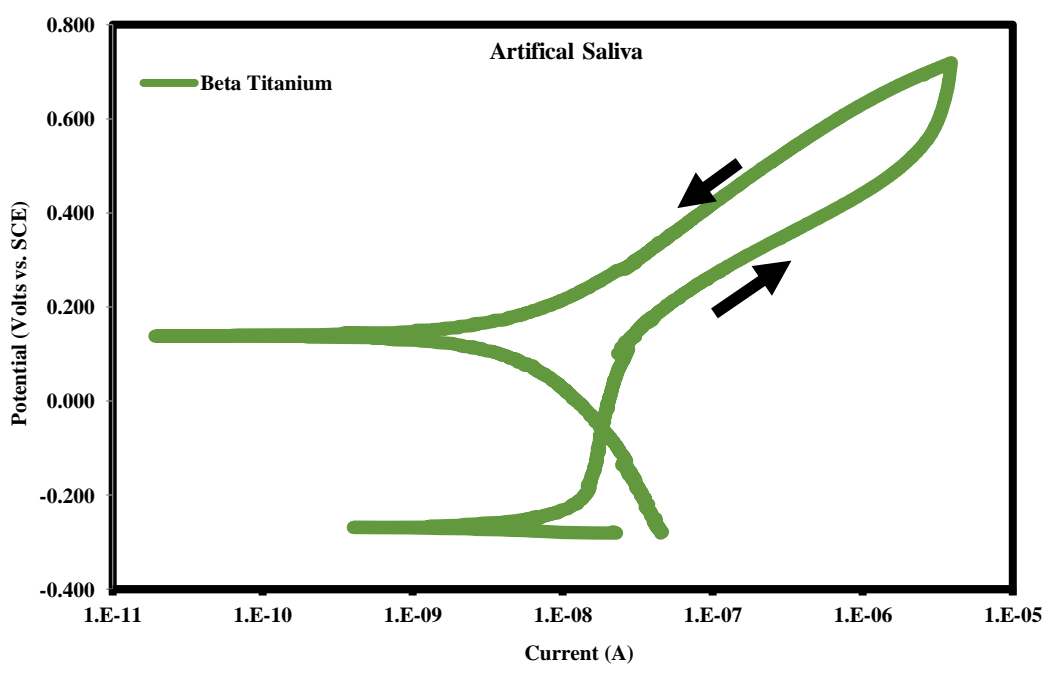


Figure 10. Potentiodynamic curve of beta-titanium wire in artificial saliva

Figure 11 shows all artificial saliva potentiodynamic curves superimposed. Pitting loops can be seen in the curves representing both gold plated wires and in the twisted stainless steel wire. Pitting is absent in the curves representing the other wires.

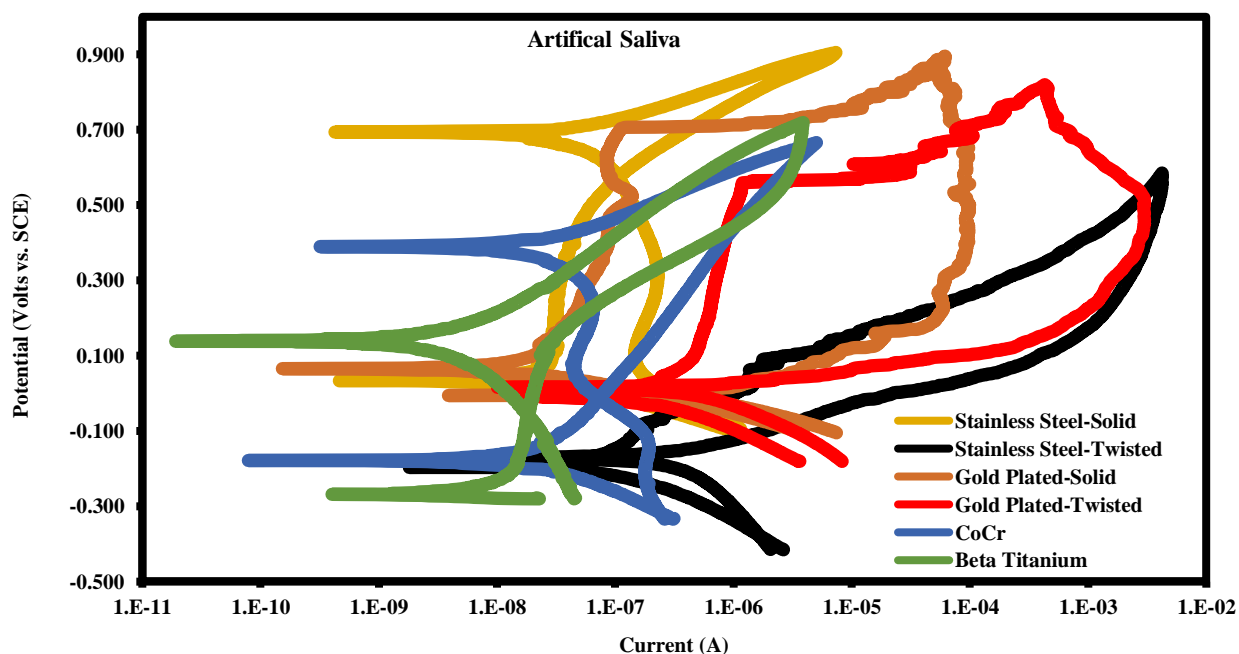


Figure 11. Potentiodynamic curves of all wires in artificial saliva

Figures 12-17 show the potentiodynamic curves representing each wire type in artificial saliva plus fluoride solution. Like in figures 5-10, these potentiodynamic curves are a graphical display of each wire type's corrosion behavior. A curve that descends to the right from its peak indicates that pitting corrosion took place, while a break to the left indicates that it did not.

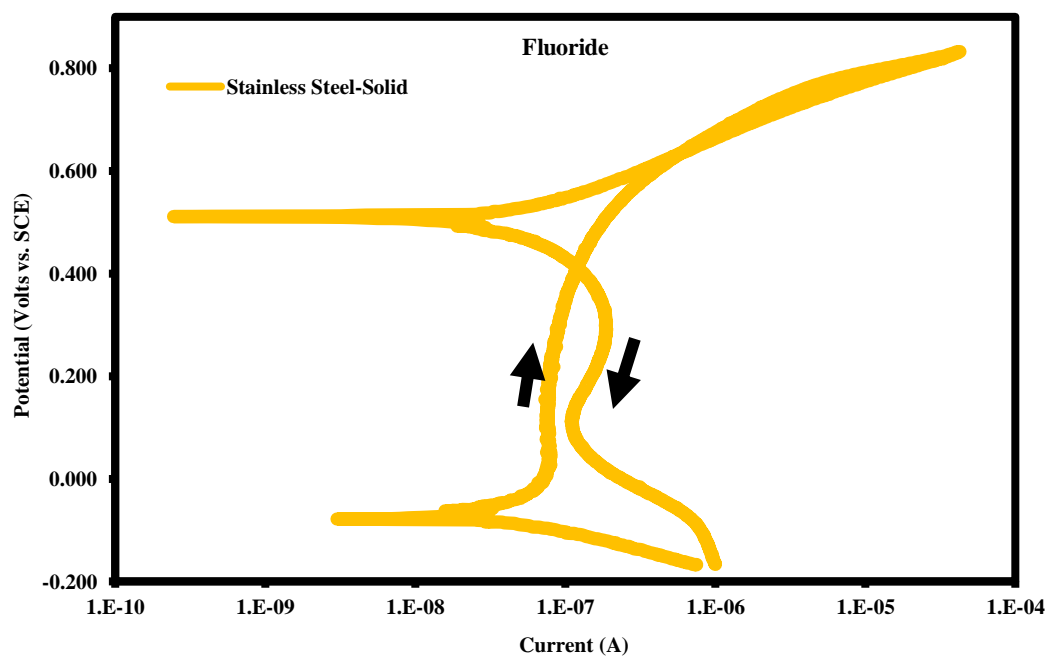


Figure 12. Potentiodynamic curve of solid stainless steel wire in fluoride solution

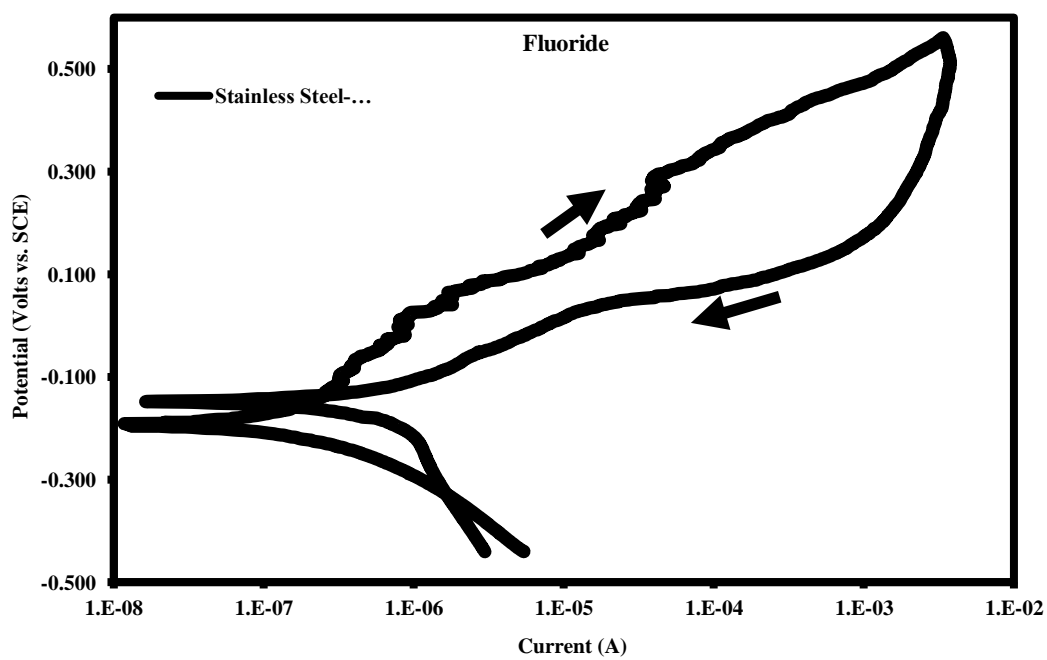


Figure 13. Potentiodynamic curve of twisted stainless steel wire in fluoride solution

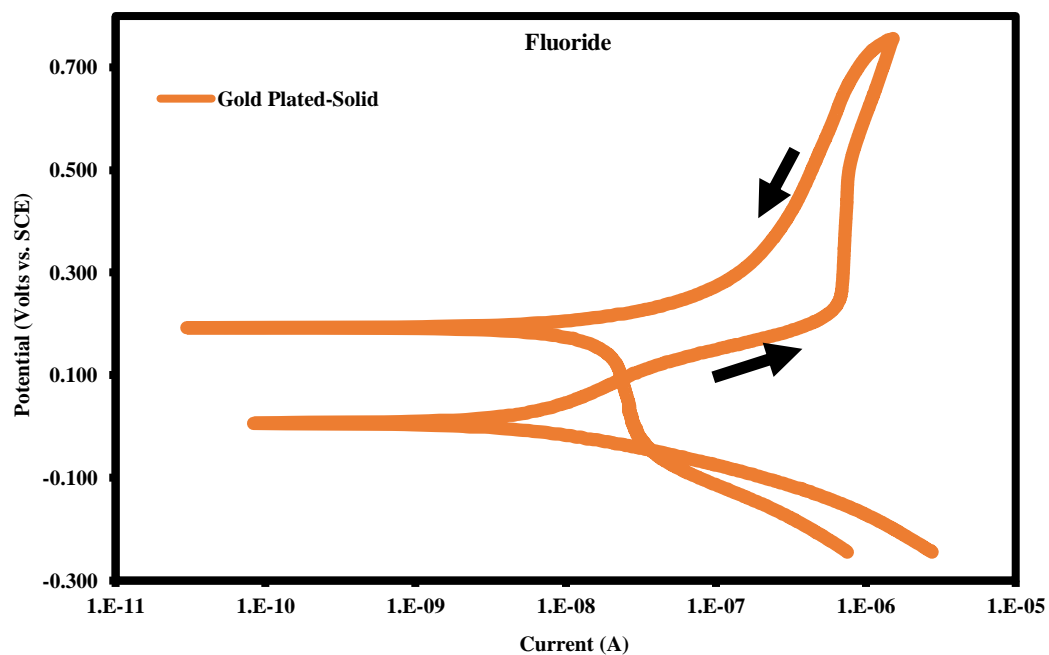


Figure 14. Potentiodynamic curve of solid gold plated wire in fluoride solution

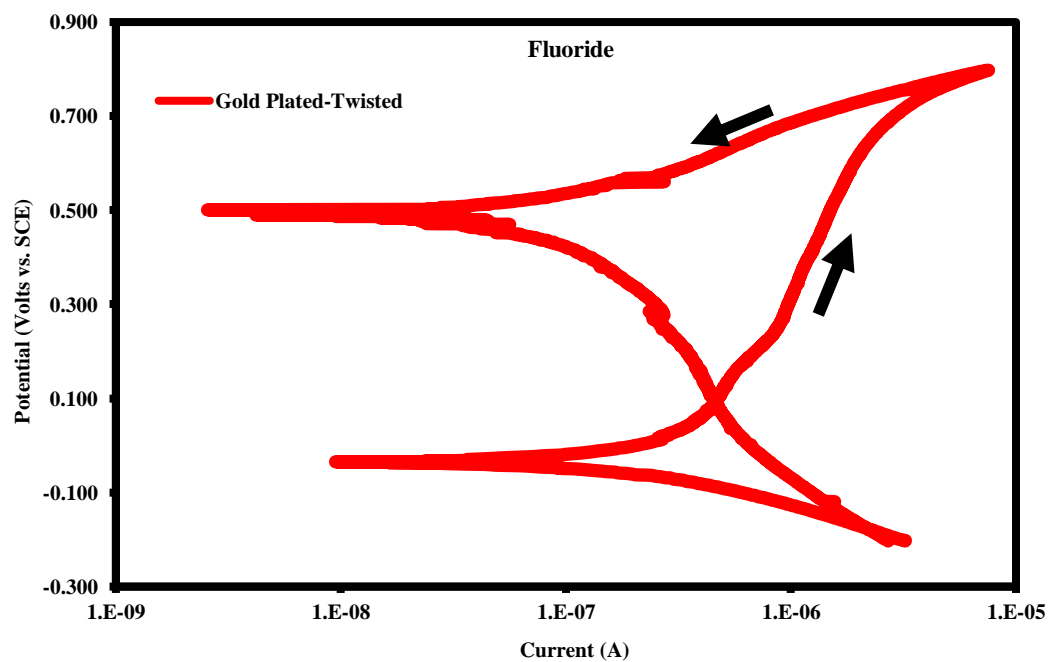


Figure 15. Potentiodynamic curve of twisted gold plated wire in fluoride solution

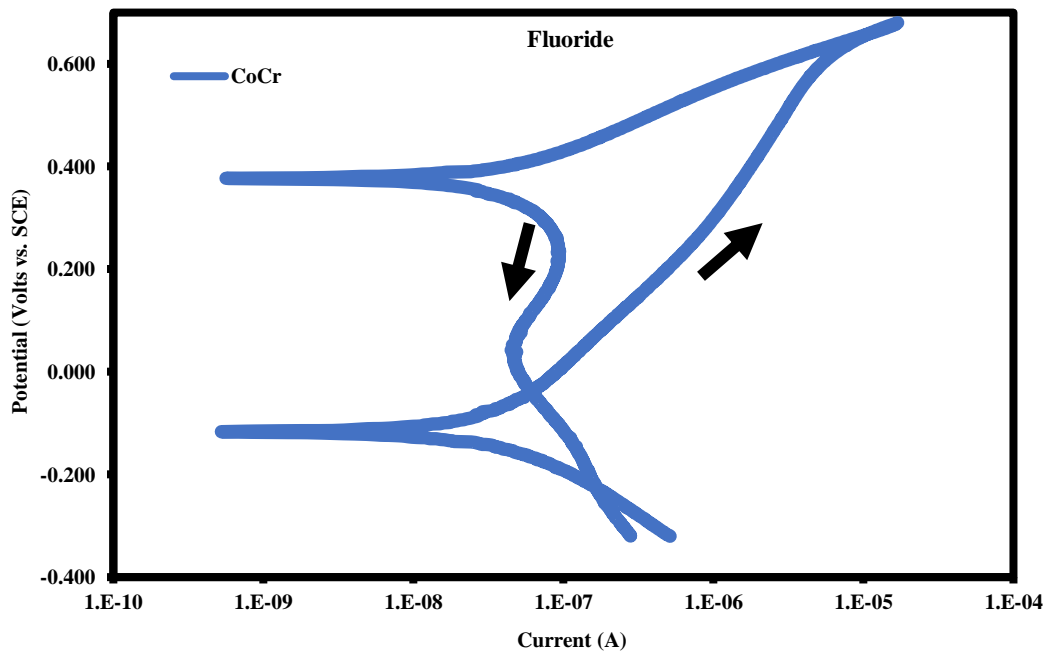


Figure 16. Potentiodynamic curve of cobalt-chromium wire in fluoride solution

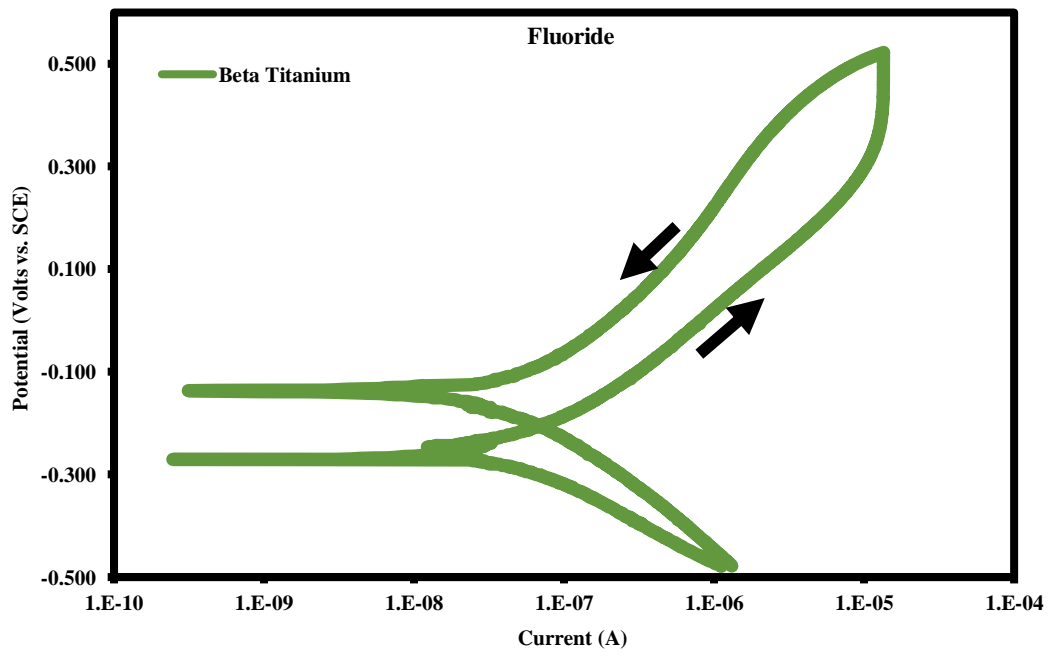


Figure 17. Potentiodynamic curve of beta-titanium wire in fluoride solution

Figure 18 shows a superimposition of all of the potentiodynamic curves in fluoride solution. A pitting loop can be seen in the curve representing the stainless steel twisted wire. Pitting is absent in the curves representing the other wires.

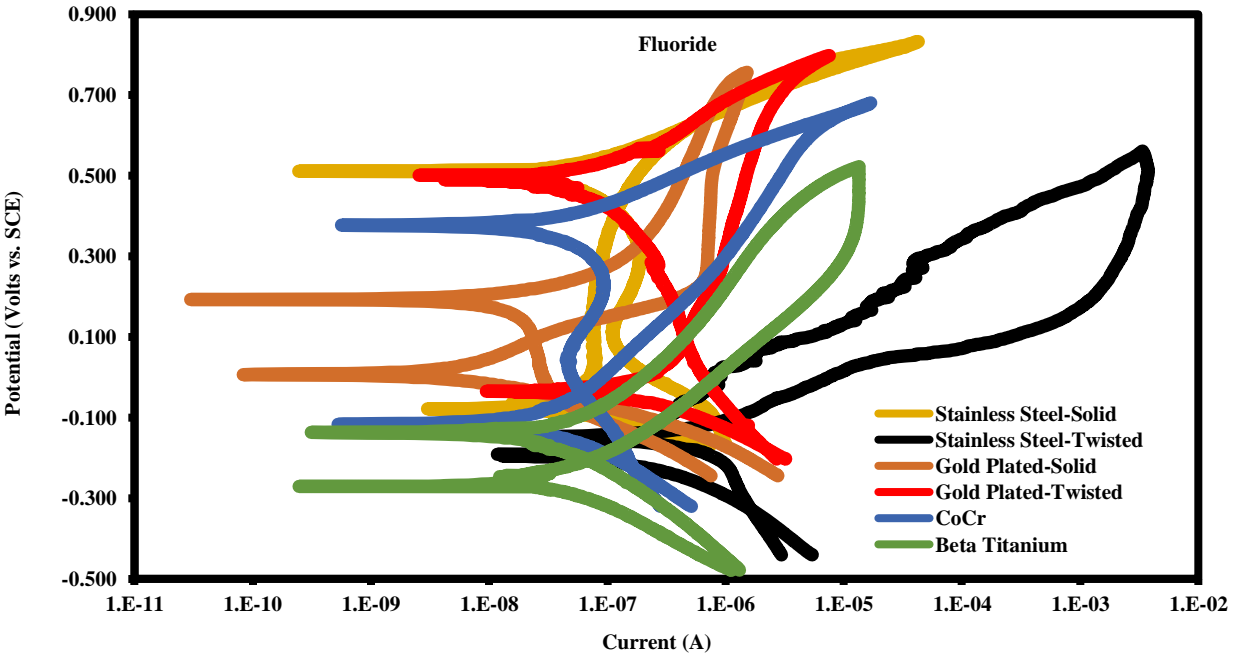


Figure 18 Superimposed potentiodynamic curves of all wires in artificial saliva + fluoride solution

CHAPTER 5 DISCUSSION

As illustrated by previous studies, orthodontic appliances are prone to corrosion when exposed to the conditions of the oral environment. An in vitro laboratory setup was used in this study to replicate these conditions so that the corrosion experienced by different fixed retainer wires could be studied. Six different wire types – solid stainless steel, twisted stainless steel, gold plated solid stainless steel, gold plated twisted stainless steel, beta-titanium, and cobalt chromium - were examined in two simulated oral environments. The first environment was artificial saliva, while the second was artificial saliva plus fluoride. Data were gathered to determine if there is a difference in corrosion rates among wire types in the oral environment with or without the presence of fluoride.

The first data point collected for each wire in this study was open circuit potential (OCP) at three hours. OCP is the electrochemical potential of a wire when there is no current flowing. Lower OCP values indicate that a wire has greater propensity to corrode. By comparing OCP levels, relative nobility of the wires can be determined. Next, polarization resistance (R_p) was measured using Gamry software as current was gradually raised. This software creates a graphical representation in the form of a line. The slope of this line is equal to R_p , with lower slopes indicating a greater likelihood for that wire to corrode. Finally, data from potentiodynamic curves was utilized to calculate corrosion current (I_{corr}). Such curves are produced by further modulating the current to which the wires are exposed. When the current rises, their state changes from cathodic to anodic at a critical point (Esmailzadeh, 2018). At this point, a passive layer is present, which is indicated by a more vertical slope in the curve. The curve eventually descends

and the direction that it breaks indicates whether or not pitting corrosion is present. A descent that breaks left indicates an absence of pitting corrosion (Ex: Figure 5), whereas a curve that breaks right indicates pitting corrosion was present (Ex: Figure 8).

At the beginning of this study, it was hypothesized that regardless of solution the twisted wires would experience greater pitting corrosion than the solid wires of similar composition due to their increased surface area and possible crevice conditions. These crevice conditions are created in the locations where the multiple strands that make up twisted wires come into contact. In artificial saliva, pitting corrosion was seen in the stainless steel and gold plated twisted wires as well as the gold plated solid wire (Figure 11). While pitting corrosion was seen in both the gold plated twisted and gold plated solid wires, the potentiodynamic curves for these two wires suggest greater pitting corrosion took place in the twisted wires. One explanation for this might be the inherent difficulty of cohesively plating a twisted wire. Plating the individual wire strands prior to twisting them might subject the gold plating to damage during the twisting process. However, plating them after twisting could leave small areas, such as near contact points, without any gold plating at all. A non-continuous or non-uniform plating along the twisted wires could result in composition differences or areas more susceptible to corrosion than solid wires whose gold plating might be more easily applied. In the artificial saliva plus fluoride solution, pitting corrosion was seen only in the stainless steel twisted wire (Figure 18).

Possibly the strongest evidence supporting the above hypothesis comes from the corrosion current data. In artificial saliva, the gold plated twisted wire had by far the highest I_{corr} value, followed by stainless steel twisted. Both values were significantly

greater than the remaining wires. The same trend continued in the artificial saliva solution with added fluoride. Although the stainless steel twisted measured slightly higher than the gold plated twisted in this solution, both values were again significantly greater than all other wires. A related factor to consider is that, when used clinically, retention wires are bonded to the teeth in multiple locations along the wire. These bonded locations become potential areas of crevice corrosion. Because multistranded wires tend to be bonded to more teeth than solid wires, a greater number of potential crevice corrosion locations are present (Maijer et al., 1982). Therefore, while a multistranded wire bonded to every anterior tooth may better maintain lower incisor alignment, clinicians must accept that it will also experience greater corrosion than a solid wire bonded only to the canines (Al-Nimri et al., 2009). The results of this study mostly agree with the above hypothesis and suggest wire conformation is something that clinicians must weigh when selecting retention wires that are meant to remain in place indefinitely.

A second hypothesis made prior to this study was that the gold plated wires would experience less corrosion than the wires comprised of other materials. Gold is commonly used for dental restorations in the oral cavity because it is relatively inert and rarely elicits hypersensitivity reactions in patients (Wiltshire et al., 1996). However, the OCP measurements showed that while the gold plated wires performed better than most wires, it was actually the solid stainless steel wire that had the highest OCP value in both solutions. In the absence of fluoride, the gold plated wires recorded the next two highest OCP values, with the solid wire measuring greater than the twisted. Conversely, when fluoride was present the gold plated twisted was second highest followed by gold plated

solid. Cobalt chromium had the lowest OCP in artificial saliva, while beta-titanium was the least noble in artificial saliva containing fluoride. The solid stainless steel wire also had the greatest polarization resistance in both solutions. In artificial saliva, beta-titanium measured the next highest followed by gold plated solid. However, when fluoride was present in solution the order went solid stainless steel, gold plated solid, and then cobalt chromium. Gold plated twisted recorded the lowest R_p value without fluoride present, whereas stainless steel twisted had the lowest R_p when fluoride was present. When looking at corrosion current, the gold plated twisted had by far the largest I_{corr} value in artificial saliva, followed by the stainless steel twisted. These two wires also had significantly greater I_{corr} values than the other wires in the presence of fluoride, although the stainless steel twisted was largest for that solution. In contrast, the gold plated solid wire had very low corrosion current in both solutions. It scored the lowest with fluoride present and second lowest without. This indicates that wire conformation plays an integral role as composition in susceptibility to corrosion. The protective gold plating, although effective in limiting corrosion current of solid wires, is unable to always overcome the corrosion prone conformation of twisted wires. When looking at the potentiodynamic curves for artificial saliva, it can be seen that pitting corrosion took place in both the solid and twisted gold plated wires, as well as the stainless steel twisted wire. However, when fluoride was added only the stainless steel twisted wire experienced pitting corrosion. The lack of pitting corrosion in gold plated twisted wires in the presence of fluoride supports the idea that gold plating helps prevent corrosion when fluoride is present. This is likely due to the fact that gold is not reliant upon a chromium related passive layer for corrosion resistance, but rather is inherently inert.

Thus, allowing gold to remain corrosion resistant when exposed to conditions in which other alloys corrode. This study's results, therefore, agree with the second hypothesis as well.

One final hypothesis made prior to this study was that OCP and R_p values would be lower, whereas I_{corr} values would be higher for respective wires in the artificial saliva plus fluoride solution than in artificial saliva alone. Sodium fluoride is a strong electrolyte and in theory would be a conductor of the electrical current to which the wires were exposed. In general, results show that this hypothesis was correct. For four of the six wires, OCP values were higher in artificial saliva alone than they were when fluoride was added. Only gold plated twisted and cobalt chromium measured more noble with fluoride present. Polarization resistance followed a similar trend with four of the six wires recording greater values in the absence of fluoride. Only the two gold plated wires recorded greater R_p values in the presence of fluoride. This again indicates that when all other factors are equal (including wire composition and conformation), gold plating helps prevent wire corrosion in the presence of fluoride. Lastly, the I_{corr} values increased for every wire except gold plated solid with the addition of fluoride to artificial saliva. That the gold plated solid wire experienced lower corrosion current in the presence of fluoride than when it was absent, strongly suggests gold plating resists the corrosive effects of fluoride and is a good option for long term retention. This is especially relevant today as most patients are exposed to fluoride from varied sources multiple times daily.

Because of the complexity of replicating the oral environment, this study had several limitations. All tests were done at room temperature instead of body temperature and there was no variation in pH or salivary contents for individual tests. In the mouth,

conditions can fluctuate based on diet and other factors. Another limitation was that only one form of fluoride additive was tested. Although sodium fluoride is the most common form that people encounter, there are several others that are commercially available. Finally, it could be argued that this study included a relatively small sample size of wires. It is possible that 10 samples per wire, per solution may not accurately reflect the true properties of each wire type.

CHAPTER 6 CONCLUSION

Although the corrosion of archwires and fixed orthodontic appliances used in active orthodontic treatment has been studied extensively, little research on this topic has been published on wires used for fixed retention. It was observed that multistranded wires experienced significantly greater corrosion currents than solid wires in artificial saliva with or without the presence of fluoride. This is relevant because they also suffer increased crevice corrosion as a result of being bonded to a greater number of teeth than solid wires. While conformation drastically impacts a wire's susceptibility to corrosion, composition was proven to be equally as important. The solid stainless steel wire recorded the highest OCP at three hours as well as the highest polarization resistance in both solutions tested. In terms of corrosion current, beta-titanium measured the lowest in artificial saliva, while gold plated solid measured the lowest when fluoride was present. The gold plated wires (solid and twisted) were the only wires whose R_p values increased in the presence of fluoride. The gold plated solid wire was also the only wire to record a lower corrosion current in the presence of fluoride than in its absence and neither gold plated wire experienced pitting corrosion when exposed to fluoride. The stainless steel twisted wire was the only wire tested whose potentiodynamic curve showed evidence of pitting corrosion in the solution containing fluoride. These observations are clinically relevant because it suggests that gold plating reduces a wire's susceptibility to corrosion in the presence of fluoride, likely due to gold not being reliant upon a chromium induced passive layer for corrosion resistance. Overall, the results of this study indicate that the addition of fluoride only adds to the harshness of the oral environment, further increasing

the susceptibility of most metals to corrosion. The importance of retention requires orthodontists to understand this when selecting the optimal wire to maintain alignment well beyond a patient's active treatment.

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