# Influence of Fluoride and Stress on the Electrochemical Properties of Nickel-Titanium Coils

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# INFLUENCE OF FLUORIDE AND STRESS ON THE ELECTROCHEMICAL PROPERTIES OF NICKEL-TITANIUM COILS

by

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# ABSTRACT
# INFLUENCE OF FLUORIDE AND STRESS ON THE ELECTROCHEMICAL PROPERTIES OF NICKEL-TITANIUM COILS

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Marquette University, 2015

The aim of this study was to examine the effects of fluoride and stress on the electrochemical properties of nickel-titanium coils. Forty Dentsply GAC NiTi coils were divided into four groups of ten and individually tested. Twenty coils were placed in a solution of artificial saliva, where ten of the twenty were compressed and the other ten were not stressed. The other twenty coils were placed in a 1500 ppm NaF solution, where ten were compressed and ten were not. The coils were connected to a computer driven potentiostat and three tests were conducted: open circuit potential monitoring for 2 hours, a linear polarization scan, and a cyclic polarization test. The results showed the coils to possess a more noble OCP when in artificial saliva compared to fluoride. The non-compressed, artificial saliva group possessed the greatest polarization resistance ($p<0.05$), while that group and the compressed, artificial saliva group displayed a significantly ($p<0.05$) lower corrosion current density. Overall, it appeared fluoride had a greater detrimental effect than did stress when considering electrochemical properties

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# CHAPTER 1
# INTRODUCTION

Orthodontics is a specialty in dentistry that involves the correction of malocclusion. Due to the relationship of the jaws to each other or just the dental arches themselves, any discrepancy can create malocclusion. Orthodontics uses force to move the teeth into proper occlusion (Proffit et al., 2007). To move teeth into their proper position, force has to be placed on the tooth to allow for physiological bone resorption on the pressure side and bone fill on the tension side (Proffit et al., 2007). This physiological bone remodeling is the basis for orthodontic tooth movement. Research has shown that light continuous force produces the most physiologic tooth movement (Proffit et al., 2007). It is a balancing act between forces being too heavy that can cause undermining resorption of the bone and forces being too light that would not produce any tooth movement. Orthodontic tooth movement is often accomplished by bonding a bracket to each tooth. A wire is ligated to the bracket. By ligating the wire to the bracket it produces a force that facilitates tooth movement (Proffit et al., 2007). Orthodontic tooth movement is not limited to brackets and wires but this method is widely used. The materials used for brackets and wires can vary, but historically brackets and wires were composed of stainless steel. Although stainless steel brackets were widely used, wires being made of titanium alloys became available in the 1970s (Proffit et al., 2007). One of these wires was a Nickel-Titanium (NiTi) alloy developed for the space program and the second wire was Titanium Molybdenum alloy (TMA), which was developed for orthodontics.

Nickel-Titanium is a very popular alloy used in orthodontics. It can be used as an archwire to help align teeth. It can also be used in a coil spring form to open and close spaces in the dental arch to help to align teeth. Its use in orthodontics is extensive and much research has focused on understanding the properties of this material. NiTi's unique properties include demonstrating shape memory and superelasticity. The basis for nickel-titanium's unique properties lies in its ability to exist in two different crystal phases. These phases are known as martensite and austenite. At low temperatures and high stress the martensitic crystal structure is most stable. At high temperatures and low stress the austenitic crystal is the most stable (Proffit et al., 2007). Although other alloys can exist in different crystal structures, NiTi is unique because this alloy can reversibly transition between the two structures at low temperatures. NiTi's ability to phase transition, or transition between crystal structures, gives this alloy the ability to exhibit shape memory and superelasticity. Shape memory is the ability of NiTi to undergo deformation at one temperature, then recover its original shape upon heating above its transformation temperature. The shape memory property gives NiTi the ability to return to its original form after being plastically deformed. NiTi is formed into a shape at a temperature well above the transition temperature in the austenitic phase. The alloy can then be plastically deformed in its martensitic phase but will return to its original form when heated back to the austenitic phase (Barwart et al., 1999). For instance, a certain shape (arch form) can be set while the alloy is maintained at an elevated temperature, when it is cooled and placed into the mouth engaging the mal-aligned teeth it is plastically deformed. As the oral temperature raises the temperature of the alloy above the transition point it returns back to its original arch form over time. The force the wire places on the brackets that are bonded to the teeth as the wire returns to its original form produces orthodontic tooth movement. Superelasticity refers to NiTi's ability to have very high reversible strain. This is also due to the martensite-austenite phase transition. In temperatures very close to but below the transition phase, stress can be placed in the austenitic phase causing transition into the martensitic phase. Over a wide range of strain, this alloy produces an almost flat section on the load-deflection curve and a steady amount of stress (Barwart et al., 1999). Clinically NiTi can be deformed at high levels and still produce a consistent amount of force.

Nickel-Titanium can be used as an archwire to align teeth but also in coil spring form to close or open space. NiTi coils have become popular because of the low and constant force it places on the teeth. The properties of shape memory and superelasticity allow the coil to be stretched over a varying distance but produce the same force regardless of change of distance. NiTi coils can be used in a variety of ways clinically.

Orthodontic space closure is not limited to NiTi coils and may be accomplished with stainless steel coils or elastomeric chains. When comparing elastomeric chain and stainless steel coils to NiTi coils, it has been shown that NiTi closes space more efficiently with light continuous force.

Since NiTi coils are a commonly used material in orthodontic treatment, it is important to understand how this material is affected by the oral environment. Often when metal or alloy reacts with the environment some form of corrosion occurs. Corrosion can be described as an electrochemical process where a metal is transformed into an oxide through the loss of ions (Akid, 2004). To simulate the oral environment in this study, compressed and non-compressed NiTi coils were tested in artificial saliva and fluoride to compare their corrosion characteristics. The results of this data will allow for better understanding of the corrosion properties of NiTi coils when in the oral environment and exposed to fluoride.

# CHAPTER 2
# LITERATURE REVIEW

Orthodontics is a specialty in dentistry that concentrates on the treatment of malocclusions. These malocclusions can be caused by irregular skeletal relationships or an irregular relationship of the dental arches to each other. To help correct these malocclusions, teeth can be moved orthodontically to allow for teeth to be placed into proper occlusion. To initiate orthodontic tooth movement forces must be placed on the teeth desired to move. This force creates a physiological change in the bone surrounding the tooth and allows the tooth to move. Orthodontic fixed appliances are often used to allow for a controlled medium to place force on the teeth. These appliances are often but not limited to stainless steel brackets bonded to the enamel surface and an archwire ligated to the brackets. The amount and direction of force influences the type of tooth movement, which can have adverse or beneficiary affects. The force on the teeth can range from heavy or light force. Some believe the use of heavy force increases the rate and the amount of tooth retraction and can produce orthopedic affects, but this also includes the adverse effects of loss of rotation control and greater anchorage loss when orthopedic affects are not desired. On the other hand, the amount of anchorage loss is proportionally less in the use of light force (Yee et al., 2009).

To correct some malocclusions, extractions of permanent teeth are necessary to create a proper balance and occlusion. This type of treatment is typically used to minimize crowding and gain appropriate occlusal relationships (Proffit et al., 2007). Once space has been created from extractions, these spaces need to be appropriately closed using orthodontic mechanics. Closure of space can be achieved multiple ways. One way involves closing loops in a continuous archwire. This wire is ligated to each bracket and is activated by pulling the distal ends of the wire enough to open the loops and cinching the wire behind the most distal bracket to inhibit the wire from sliding anteriorly. The force from the activated loops closes the extraction space up to the point where the loop is no longer open or active. Another method of closing space is termed sliding mechanics, which involves pushing or pulling a tooth along a continuous archwire with a force delivery system adequate to produce and sustain movement. Generally, either a coil spring or a form of elastomeric material is used to accomplish tooth movement (Barlow and Kula, 2008).

The alloy NiTi was first introduced for use in orthodontic treatment as a result of the discovery of its unique characteristic of shape memory. The shape memory characteristic of NiTi alloys is due to the occurrence of two crystal modifications, called austenite (high temperature phase) and martensite (low temperature phase), which can be changed back and forth through variations in temperature (Barwart et al., 1996). The transition between different phases (crystal structures) for NiTi occurs during the transition temperature range (TTR) (Nattrass et al., 1997). During this temperature range the two crystal forms exist in equilibrium. The two phases are characterized by different physical properties. Martensitic wires are highly ductile and may be plastically deformed. When heated to its TTR, such a deformed wire returns to its original shape (shape memory) (Barwart et al., 1999; Miura et al., 1988). The advantage of shape memory lies in the ability of ligating a NiTi archwire with an ideal form, in an arch with an undesirable arch form. The force from the wire returning to its original form is placed on the teeth and allows for the movement of those teeth to the desired arch form. Another unique characteristic NiTi can also express is called superelasticity. Superelasticity refers to the characteristics of the wire that influence stress and strain. Strain refers to the amount of deformation at distinct intervals of tensile or compressive loading (stress). In regards to superelastic NiTi, in spite of the increase of strain placed on the material, only a relatively small increase of stress occurs. This superelastic phenomenon is caused by the bending elastic energy, which is a stress-induced martensite transformation (Miura et al., 1988; Manhartsberger and Seidenbusch, 1996). This phenomenon is reversed when strain is reduced and can only occur at temperatures above the TTR. When examining the stress strain curve of a superelastic wire, one can see a plateau phase along the deflection of the wire, which reflects the constant force delivery. Brauchli et al. (2011) make the point that when plotting the stress vs strain curve for stainless steel (SS) springs, it displays a linear plot of force deflection unlike the force plateau of NiTi. Brauchli et al. (2011) also state that the plateau is due to a structural lattice shift from austenite to martensite in the activation curve and vice versa in the deactivation curve. The deactivation portion of the curve is the most important to orthodontics because it is the force delivered clinically. The energy that was stored in the lattice by transforming austenite to stress induced martensite is continuously released during deactivation and leads to the maintenance of the force level even though the spring is being deactivated (Brauchli et al., 2011). The advantage of a superelastic NiTi spring is its ability to provide consistent force delivery.

NiTi coils are often viewed as an efficient way to close spaces but can also be used in other ways for orthodontic tooth movement in correction of malocclusion. Aksoy and Aras presented a case report of correcting partially impacted second molars. During the first phase of orthodontic treatment a lingual arch was constructed and a NiTi coil spring was attached to the arch and to the partially impacted second molar (Aksoy and Aras, 1998). The force placed on the tooth from the NiTi allowed for eruption of the second molar and continued orthodontic treatment allowed for the correction of the patient's malocclusion. NiTi coil springs can be used to close space (closed coil springs), as well as open space between teeth (open coil springs). Binder's case report states that open coil springs are often placed over archwires to open space for blocked out teeth or for other purposes. Binder used a method of compressing an open coil spring between two brackets that are a distance apart that is smaller than the original size of the coil. Once the coil is placed, the "opening" force of the coil leads to force placed on each tooth and the opening space for a blocked out tooth (Binder, 2002). Ozturk et al. (2005) used open coil NiTi springs to distalize molars. If a patient presents with a Class II malocclusion, one way to correct it is to distalize the maxillary posterior segment and allow the molar to occlude in a Class I occlusion. Although this method seems simple, anchorage loss can occur when opening space at the area of the anterior teeth. Anchorage loss occurs when the force that is needed to move the posterior teeth is greater than the force needed to move the anterior teeth, which is an undesired movement. Ozturk et al. (2005) found that distalization occurred from distal tipping of the molar and anterior positioning of the premolars. Their results showed that by using the NiTi open coil springs for molar correction, that for every mm of distal molar movement, the premolars (right and left) moved anterior .56 mm and .68 mm (Ozturk et al., 2005). Carillo et al. (2008) presented a case report using closed coil NiTi springs to intrude teeth. Intrusion of teeth may be desired if a tooth is over erupted and causes a disturbance in the vertical dimension of the occlusion. In Carillo et al.'s study, a miniscrew was placed in the alveolar bone and a closed coil spring was attached to the screw and the desired molar for intrusion. The force of the closed coil spring on the tooth and the absolute anchorage of the miniscrew allowed for intrusion of the molar (Carillo et al., 2008). There are more examples of NiTi coil springs versatility being used to retract teeth into space, open spaces in the arch (Steinbech et al., 2006), and distalize molars (Schneevoigt et al., 1999).

Although NiTi has ideal characteristic for orthodontic tooth movement, it is important to understand the force placed on the teeth. In Ryan's review of NiTi coils he states that light continuous forces have been considered optimal for tooth movement. He goes on to say that light forces produce a continuous tooth movement that takes less time (Ryan, 1995). Suzuki et al. (2006) studied tooth movement created by various titanium coils. In regards to light forces in orthodontic tooth movement he states that the degree of periodontal tissue compression influences the pattern of bone resorption, leading to the pattern of tooth movement. Moderate compression leads to direct bone resorption in periodontal tissue, and excessive compression leads to undermining bone resorption. Lighter forces are advantageous for tooth movement without inducing tissue damage (Suzuki et al., 2006)). Nattrass et al. (1997) studied force systems and quoted previous literature stating that 100-200 g is optimal for canine retraction. They also comment on other theories, that the duration of applied force is more influential than the actual magnitude of the force. They go on to say that light continuous forces seem to have a more advantageous physiological result, while heavy momentary forces are not effective in bone remodeling (Nattrass et al., 1997). In a study by Bokas and Woods, they used a split mouth design study to compare closing rates of NiTi coils versus elastomeric chains for premolar extraction sites. They state that forces in the range of 100-300 g specifically for canine retraction are typically found to be ideal. They then go on to say that this range could change due to the morphology of the teeth (Bokas and Woods, 2006). In regards to orthodontic tooth movement, light continuous forces are advantageous for a physiological response, but when closing extraction spaces the ideal force range can increase depending on the size, shape and amount of teeth being moved at the time (Espinar-Escalona et al., 2013).

There are a number of variables that affect the force coil springs deliver to teeth. These include the type of alloy, wire size, lumen size, pitch of the coils, temperature and the length of the spring (Boshart et al., 1990). Boshart et al. (1990) studied the forces of Co-Cr-Ni and stainless steel open and closed coil springs. The coils varied in composition, type, length, wire size, and lumen size. Their results showed that an increase in wire size increases the load deflection rate. As the angle between the coils that are perpendicular to the long axis of the spring, also known as pitch angle, increases, the load deflection rate increases due to the decrease in coil length. The results also showed Co-Cr-Ni being less stiff than stainless steel. Bourke et al. (2010) found that as the pitch of a wire decreases the amount of the wire incorporated into the wire is increased. Chaconas et al. (1984) tested force characteristics of various open coil wire types with various wire and lumen sizes. They found that an increase in wire size and a decrease in lumen size would increase the maximum force production and the force produced by a given activation. Angolkar et al. (1992) tested Co-Cr-Ni, stainless steel, and NiTi closed coils springs for force degradation. The coils were extended to a force level of 150-160 g. The coil forces were tested at eight time intervals within 28 days. The study revealed that over time all three coil types showed force loss. The least amount of force decay was found in one of the groups of NiTi coils but overall force loss was in the range of 8 to 20% (Angolkar et al., 1992). von Fraunhofer et al. (1993) compared the unloading force of open and closed NiTi and stainless steel coils. The results showed that open coil NiTi springs showed a force of 61 g over a range of 7 mm in activation. The stainless steel open coil spring showed a force of 257 g to 191 g over a change of 0.3 mm in activation. Overall, the NiTi coils showed light continuous (75-100 g) force over a range of activation, while the stainless steel coils delivered heavy forces with rapid decay over small activations (von Fraunhofer et al., 1993). Espinar-Escalona et al. (2013) studied the effects of temperature on the force application of NiTi closed coiled springs. Coils were tested under tension in room temperature artificial saliva. As the coils were unloaded the solution temperature was either increased or decreased. The results showed that changes of temperature did not modify the superelastic behavior of the NiTi coils and that an increase in temperature of the solution decreased the corrosion potential (Espinar-Escalona et al., 2013).

Although NiTi coil springs appear to be a sufficient mode for closing space it is important for clinicians to understand other products on the market. Coils are not the only method available for closing space as stated above. One main comparison occurs between NiTi coil springs and elastomeric chains. When comparing these products it is important to understand their force delivery. When these materials are stretched, their stress increases proportionally to the applied strain. This reaction is also described as the material’s elastic modulus (Nightingale and Jones, 2003). When the stretching is released (unloaded) the decrease in strain is identical to its previous increase, this is known as a perfectly elastic material. Nightingale and Jones found that elastomeric chains do not show this exact characteristic. When an elastomeric chain is stressed, it loses energy and its unloading curve displays less stress for a given stretch compared to the loading curve of NiTi. Nightingale and Jones also performed a randomized clinical trial with twenty-two orthodontic patients using a split mouth design. They closed space on one quadrant with a sliding elastomeric chain and sliding mechanics. On the opposing quadrant, they used a nickel-titanium coil spring and sliding mechanics. Initial forces were recorded as well as at the subsequent visit. It was found that 59% of the elastomeric chains maintained at least 50% of their initial force over a period of 1-15 weeks. NiTi coil springs lost force rapidly over the initial 6 weeks with a force level plateau for the remainder of the time. Comparatively, 46% of the NiTi coils maintained at least 50% of their initial force. The monthly rate of space closure for elastomeric chains was 0.21mm and 0.26 mm for NiTi coils. Nightingale and Jones concluded that elastomeric chains and NiTi coil springs close space similarly (Nightingale and Jones, 2003). Bokas and Woods performed a clinical comparison of elastic chains and NiTi springs through a split mouth design. Initial forces of the chain and springs were equal and anchorage loss was measured. One of the major findings was that elastic chains have been shown to lose approximately 50-70 percent of their initial force over the first 24 hours. Bokas and Woods state that the force decay then becomes more gradual, resulting in approximately 30-40 percent of the original force remaining after four weeks. To many practitioners this is a significant amount of force loss if trying to retract teeth over time. If an appropriate amount is placed on a tooth during placement of the elastic chain for orthodontic tooth movement, it is unknown how effective the decaying force is during this 4 week time period. Their results showed no statistical difference in anchorage loss (forward movement of the molar) or space closure (Bokas and Woods, 2006). Samuels et al. (1993) also did a study comparing the rate of space closure using a NiTi spring and elastomeric chain. They also used a split mouth design study comparing elastic chain and NiTi coils and found that there was a significantly greater rate of space closure by the NiTi closed coil spring. Samuels et al. found that the NiTi springs offered a more ideal elastic modulus and displayed a low constant force that was more biologically acceptable. The elastic chain delivered high intermittent forces with rapid force decay (Samuels et al., 1993). Santos et al. (2007) compared the force decay between NiTi springs and elastomeric chains. Santos et al. stated the elastomeric chains exhibited a high percentage of force loss during the first 24 hours, but after that the force decay continued progressively, while the NiTi coil springs displayed progressive force decay over 28 days. These findings are important because it is essential for practitioners to understand the amount of force being used even while the patient is out of the office setting. Sonis also compared the rate of canine retraction between elastomeric chains and NiTi springs and found NiTi springs to be more favorable in regards to the rate of space closure (Sonis, 1994).

Additional comparisons have been made between NiTi coils and repelling magnets. For correction of malocclusions, molars can be distalized to achieve the appropriate molar classification. Erverdi et al. (1997) compared repelling magnets and open coil springs to distalize molars. One significant finding from this study was the force decay found with the magnets. As the magnets moved farther away, the force decreased. Erverdi et al. stated that at 0 mm, the force generated was 225 grams, but at a distance of 1 mm apart, the force value was 75 grams. The force decay was 50-70 percent for every 0.5-1 mm of tooth movement. This type of force decay was not observed in the coil, which displayed more distal tooth movement and was found to be a more effective means of molar distalization (Erverdi et al., 1997).

Although the characteristics of NiTi springs have been widely studied, Maganzini et al. (2010) found that not all NiTi coil springs manufactured were created equal. The commercial coils they tested showed inconsistent unloading forces and failed to exhibit characteristics like peak forces and constant deactivation force. Melsen et al. (1994) also tested 19 different coil springs and found only the GAC spring exhibited the desired superelastic characteristic in the deactivation curve.

Much of the literature points to NiTi springs having a possible clinical advantage over other conventional alternatives. If a clinician decides to choose NiTi springs, it is important to understand any possible variation that may occur in the oral environment. Han and Quick performed a study where they compared the force generation of stainless steel springs, NiTi springs and elastic chains after being exposed to a simulated oral environment. They found that NiTi springs were highly resistant to degradation in the simulated oral environment. Stainless steel springs had some degradation and elastic chains lost the largest fraction of force compared to the other 2 groups (Han and Quick 1993). Although NiTi springs do show a lack of degradation in the oral environment, it is important to understand any changes that may occur while the spring is active in the mouth. Tripolt et al. (1999) tested superelastic coil springs in various temperatures in the mouth. At extreme temperatures, superelastic coils are very sensitive and can display varying force ranges. Tripolt et al. stated that although in varying extreme temperatures the force magnitude of the coils greatly varied, they found that in the range of 30-40$^{o}$C, the force magnitude variation was very small. Vidoni et al. (2010) examined the superelastic characteristics of coils Nitinol, NiTi, and RMO coils after exposing them to strain and thermal treatments. These coils were kept in artificial saliva and thermocycling was performed twice on days 22 and 45. Only the Nitinol group showed minimal changes in the superelastic phase or load deflection. None of the groups had changes in their mechanical properties. Nattrass et al. (1998) compared elastomeric chains and NiTi springs in varying oral environments including Coke, turmeric and increased temperatures. The results showed elastomeric chains were affected by both environment and temperature. Temperature caused the greatest amount of force loss of the two (Vidoni et al., 2010). On the other hand, NiTi springs were not affected by their environment and demonstrated a slight increase in force as temperatures increased. To counter these results, Walker et al. (2005) tested the effects of fluoride prophylactic agents on the mechanical properties of NiTi archwires. These fluoride agents can often be found in the oral environment. The results showed a decrease in the unloading properties of NiTi wires.

Like any metal, an alloy can experience corrosion from its surrounding environment. Corrosion can be referred to as environmental degradation or even rusting. This process can be defined as “chemical wasting” for when a metal or alloy reacts within its environment (Akid, 2004). Alloys like NiTi can exhibit pitting corrosion where localized metal is lost due to ionic migration due to the potential gradient between the pit and the environment. When alloys are placed in certain environments, degradation (corrosion) can occur which could lead to fracture of the alloy. Akid refers to a phenomenon known corrosion fatigue or stress corrosion cracking where a metal exhibits cracking under the combination of corrosion and tensile stress, when fatigue would not have occurred if stress or the environment were applied in isolation (Akid, 2004). When NiTi exhibits this type of corrosion, it can be concerning during active orthodontic treatment. Yokomaya et al. (2002) studied the fracture mechanisms of titanium screws for dental implants. They examined the factors that caused the acceleration of corrosion and fatigue. It was concluded that titanium may experience hydrogen embrittlement. This phenomenon can be associated with the formation of a brittle hydride phase when an alloy absorbs hydrogen from its surrounding environment. The study found that plastic deformation of the screw (metal) can accelerate absorption of hydrogen. When hydrogen is absorbed it is trapped between the interstitial site of the lattice atoms. This leads to the induction of grain refinements and/or hydride formation and causes marked reductions in ductility (i.e. the metal become brittle) (Yokomaya et al., 2001 and 2002). Yokomaya et al. also did an additional study to examine the degradation and fracture of NiTi alloys in fluoride solutions. In this study a tensile test was performed on the NiTi wires after being immersed in the fluoride environment. Additionally, the amount of hydrogen absorbed was determined. Yokomaya et al. found that one reason Ti alloys can fracture in the oral environment was due to the absorption of hydrogen in a fluoride solution (i.e. prophylactic agents) (Yokomaya et al., 2003). This information is vital in understanding what happens when NiTi is placed in the oral environment and the possibility of the material failing while being actively used in fluoride containing solutions.

The objective of this study was to examine the effect of fluoride and stress on the electrochemical properties of NiTi coils. By collecting this information, a better understanding of how these coils hold up in the oral environment will be found and if changes need to be made with treatment protocol.

# CHAPTER 3
# MATERIALS AND METHODS

Nickel-Titanium open coil springs (Sentalloy 200 gram; Dentsply GAC, Islandia, NY) were evaluated for their electrochemical properties. Ten coils were used for each test group (4 groups). These groups were divided into non-compression and compression. Within these two groups, 10 coils were tested in artificial saliva or NaF solutions. The artificial saliva solution is known as Fusayama-Meyer solution and was made up of 0.4 g/L KCl, 0.4 g/L of NaCl, 0.6g/L of $CaCl_2$, 0.69 g/L of $NaH_2PO_4$, 0.005 g/L $Na_2S{\cdot}9H_2O$, and 1 g/L of urea. The NaF solution was 1500 ppm fluoride (Fisher Scientific, Pittsburgh, PA). Both of the solutions were kept at $37^oC$ at all times. The non-compression testing consisted of a 0.020" gauge stainless steel (SS) wire weaved through the first coil of the spring. The interface of coil and stainless steel wire as well as 8 mm of the coil was painted with nail polish to avoid galvanic effects. A sheet of plastic (2 in. x 2 in. x 5 mm) was used for holding the electrodes and consisted of a hole to allow the SS wire to be feed through the plastic and allow the coil spring to be exposed to the solution. The SS wire attached to the coil was attached to an electrical connection for testing. Additional holes were placed in the plastic to allow for a graphite rod that served as a counter electrode and a saturated calomel electrode (SCE; Gamry Instruments, Warminster, PA) was used as the reference electrode. All three of the electrodes were attached to a computer-driven potentiostat (PC3; Gamry Instruments) to allow for the electrochemical testing. The non-compressed coils were tested in this set up with 10 exposed to artificial saliva solution and 10 exposed to NaF solution.

The compressed coil set up consisted of a 0.020" gauge stainless steel wire weaved through the first coil of the spring. Nail polish was painted on the interface of the

SS wire and the coil up to 8 mm from the interface down the spring. The stainless steel wire was placed through the plastic sheet to allow for exposure of the coil to solutions and for an electrical connection to be made to the coil. An acrylic cylinder was fabricated to allow the coil to be placed in the cylinder and compressed when tied to the plastic sheet by an additional plastic tie. Holes were placed in the cylinder to allow for the solution to be exposed to the compressed coil. Additional holes were placed for the reference electrode and counter electrode identical to the non-compression set up. The three electrodes were connected to a computer-driven potentiostat to allow for electrochemical testing. The compressed coils were tested with this set up with 10 being exposed in artificial saliva and 10 being exposed to NaF. Figures 1-4 display the coils and associated hardware for testing with and without stress.

The computer-driven potentiostat allowed for 3 types of electrochemical testing: open circuit potential, linear polarization and cyclic polarization. Open circuit potential testing consisted of a 2 hour monitoring of the open circuit potential. The potential at the end of the 2 hours was the comparative parameter. The linear polarization test consisted of measuring the current while the potential of the coil was scanned at 0.05 mV/s from -20 to +25 mV vs OCP. The result of the linear polarization gives the polarization resistance ($R_p$) of the coil or how easily the alloy undergoes oxidation during application of an external potential. The cyclic polarization test consisted of measurement of the current while the potential of the coil was scanned at 1 mV/s from -300 to 700 to -300 mV vs OCP. The corrosion current may be determined which indicates corrosion rate as well as the potential at which a passive layer degrades and the tendency to exhibit pitting corrosion. The OCP at 2 hours, polarization resistance, and corrosion current were compared utilizing ANOVA and a post hoc Least Significant Difference (LSD) test using a 0.05 significance level.

Figure 1. NiTi coil and acrylic cylinder

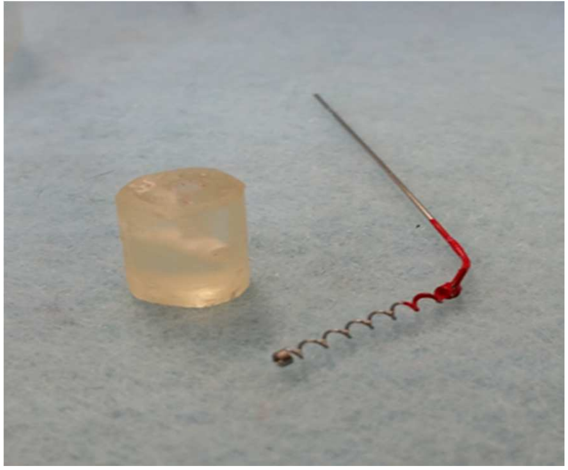


Figure 2. NiTi coil compressed in cylinder

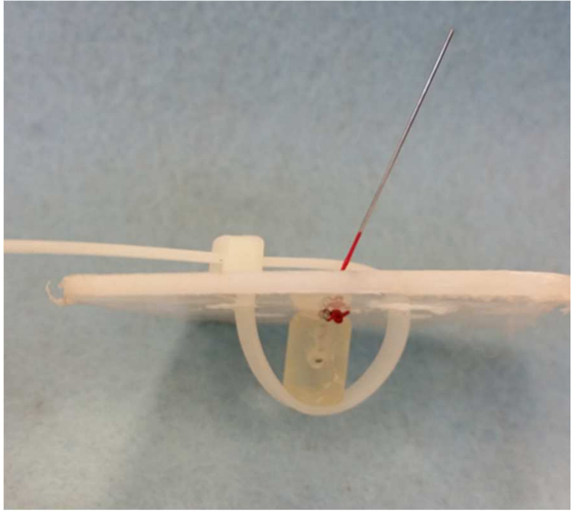


Figure 3. NiTi coil in non-compressed setup

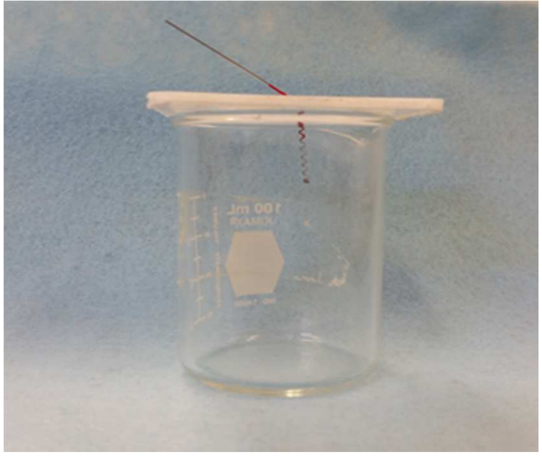
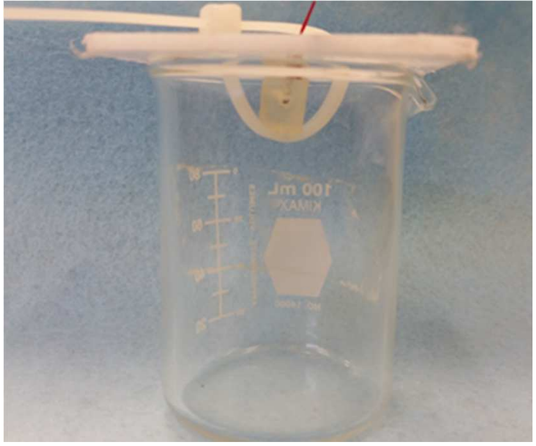


Figure 4. NiTi coil in compressed setup



# CHAPTER 4
# RESULTS

Table 1 shows the mean OCP, polarization resistance, and corrosion current for the four groups of coils. Figures 5-7 display typical curves for each of the three electrochemical tests, OCP, linear polarization, and cyclic polarization, respectively.

Table 1. Mean ± SD (Standard Deviation) for electrochemical measurements

| Coil Group | OCP @ 2 hrs (mV vs. SCE) | $R_p$ (MΩ) | $I_{corr}$ (nA) |
|---|---|---|---|
| Compressed, Fluoride | -232±46 C | 2.6±1.4 B | 17.45±7.18 B |
| Compressed, Artificial Saliva | -74±15 A | 15.5±4.1 B | 4.26±1.48 A |
| Not Compressed, Fluoride | -321±48 D | 1.6±1.2 B | 40.38±18.65 C |
| Not Compressed, Artificial Saliva | -160±37 B | 89.4±37 A | 0.60±.23 A |

Different letters denote significant differences ($p<0.05$) between coil groups.

Significant ($p<0.05$) differences were observed between all groups with respect to OCP. A greater OCP represents electrochemical nobility and it is apparent that the coils have a greater OCP in the artificial saliva solution compared to the NaF solution. Further, when the coils were compressed, the OCP was greater within the same solution. For polarization resistance, the Not Compressed, Artificial Saliva group possessed a significantly ($p<0.05$) greater $R_p$ compared to the other three coil groups, which were statistically the same ($p>0.05$). A greater polarization resistance is desirable and the group without fluoride and without compression showed a superior value. Significant ($p<0.05$) differences were also found in corrosion current, with the coils in artificial saliva having a lesser corrosion rate. In the fluoride solution, the compressed coils exhibited a significantly ($p<0.05$) lower corrosion current. In evaluating Figure 3, none of the coils showed a pitting corrosion tendency or a distinct breakdown potential.

Figure 5. Open Circuit Potential monitored for 2 hours

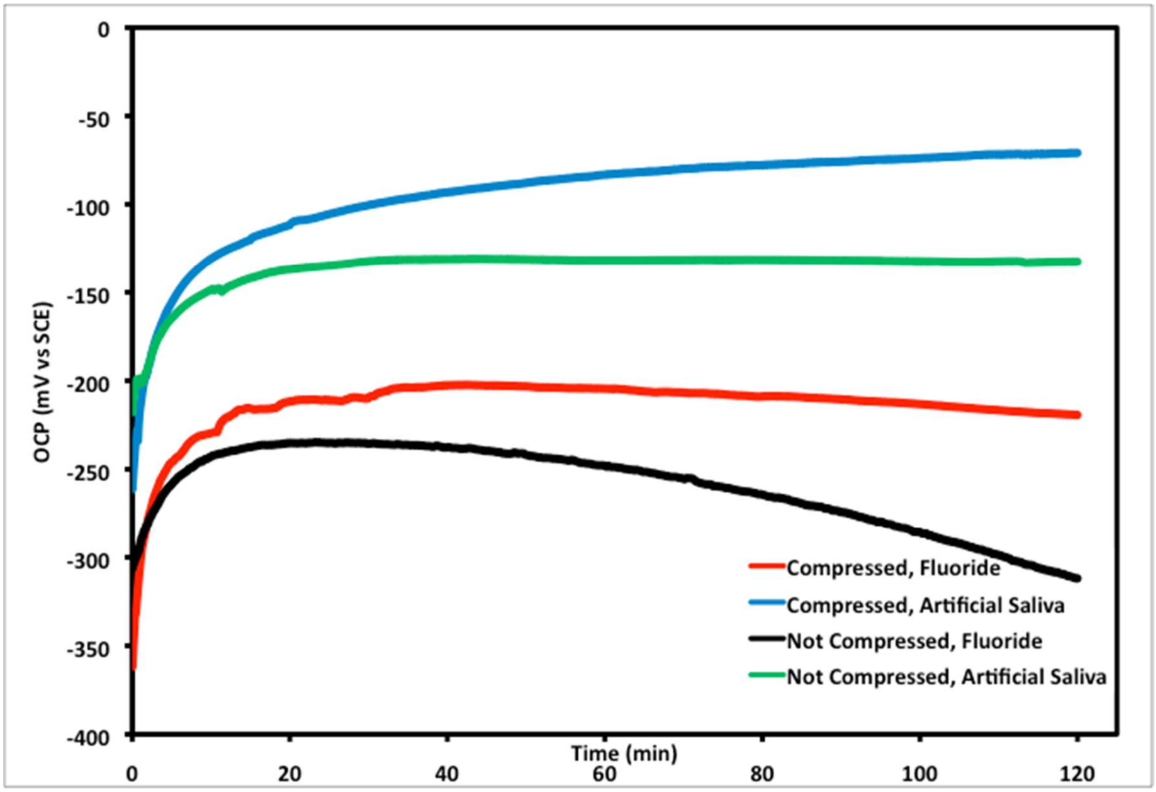


Figure 6. Comparison of typical Linear Polarization tests

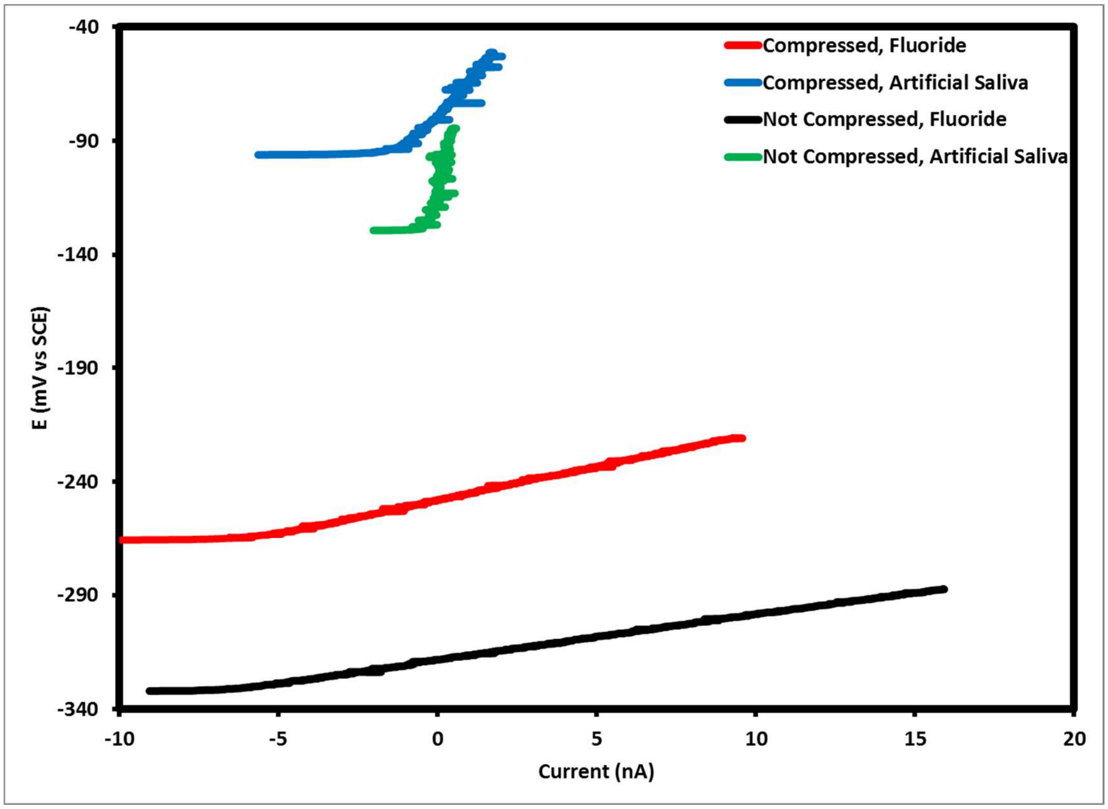
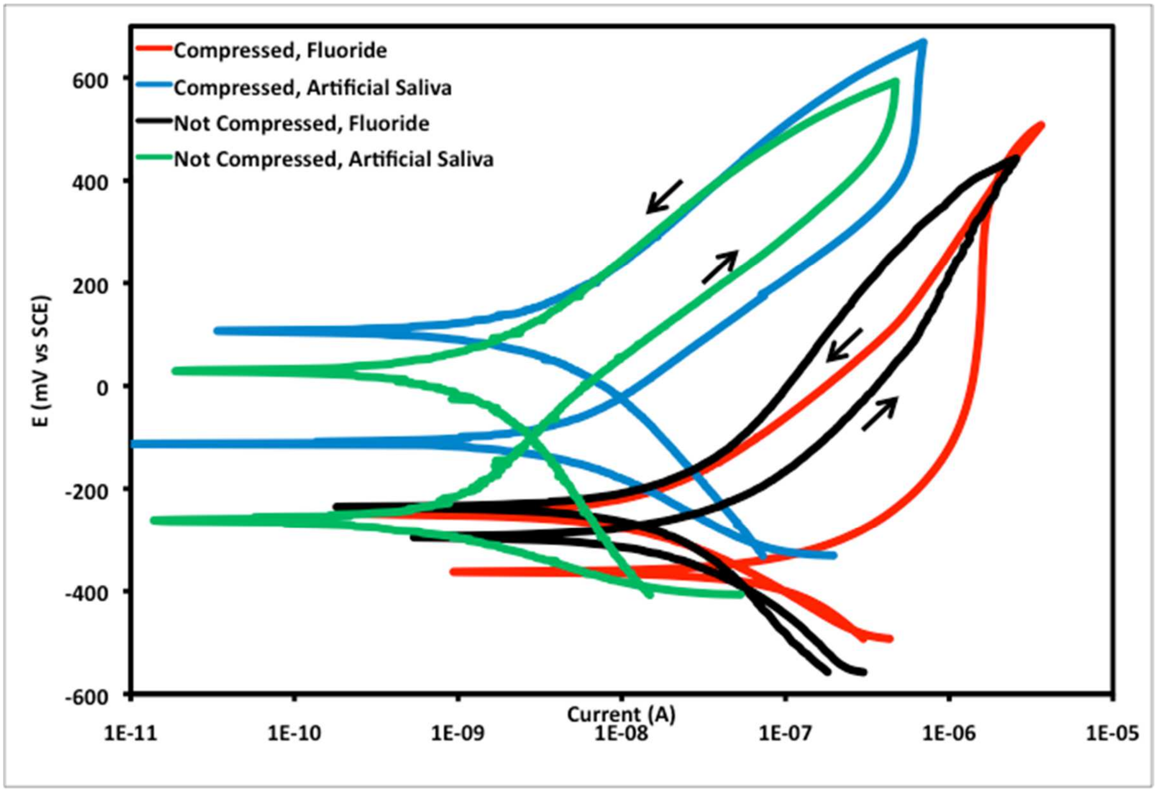


Figure 7. Cyclic Polarization comparison among groups



# CHAPTER 5
# DISCUSSION

Corrosion is the active breakdown of metal by a chemical or electrochemical reaction with its environment. Due to the electrochemical nature of corrosion, electrochemical methods are a useful way to study the corrosion of metals. The computer driven potentiostat tested the NiTi coils' corrosive behavior in varying environments through three tests. The first test run was the 2 hour open circuit potential. When comparing different metals in identical environments, the metal with the lowest open circuit potential is more likely to corrode. The second test was linear polarization. The linear polarization test gives the polarization resistance of the metal. The polarization resistance is the ratio of the applied potential and the resulting current level. If a metal's polarization resistance is higher, that means it is less likely to be polarized. The less likely it is to polarize, the less likely it is to corrode. The measured resistance is inversely related to the corrosion rate. The third test was cyclic polarization. The cyclic polarization measures the pitting tendencies of a specimen in a given metal solution system. It also is used to calculate the corrosion rate, which represents the amount of electrons being lost. A larger corrosion rate leads to a greater amount of ion loss, and a higher amount of corrosion tendency.

When comparing the coils in fluoride to those in artificial saliva, it appears the fluoride did have an effect on the corrosive properties of the coil regardless of compression or not. The artificial saliva groups had the lowest corrosion rates, the greatest polarization resistance, and greatest OCP. Thus, fluoride exposure may have some negative consequences on the coils, at least in terms of ion release. Nakagawa et al.

(2001) conducted a similar study where they tested the corrosive behavior of pure titanium and titanium alloys in fluoride containing solutions. The results showed that the pure titanium and two of the other titanium alloys showed significant corrosion, even in lower fluoride concentrations. They did note that one alloy with palladium did show resistance due to its ability to coat the surface of Ti and help resist corrosion. Similar studies by Reclaru and Meyer as well as Schiff et al. found fluoride to have a corrosive effect on titanium alloys (Reclaru and Meyer, 1998; Schiff et al., 2002; Yokoyama et al., 2003).

When comparing the compressed and not compressed coils in solution, the results show that the coils that were not compressed generally had greater corrosion currents or corrosion rates compared to the compressed coils within the same solution. Typically it is considered that stress increases corrosion of materials. Liu et al. (2011) studied the effect of loading force on the dissolution behavior of NiTi wires in artificial saliva. Their study found that bending of the wire influences the nickel release from the material. In this study it appears to be the opposite. It is possible that when the coils were compressed, this decreased the exposed surface area of the coil which ultimately decreased the amount of corrosion possible.

The comparison of compression and no compression as well as artificial saliva to fluoride did reveal differences in corrosive behavior. Overall, fluoride appeared to have more of an effect on increasing corrosion than did stress. This may support the above theory that compression decreasing the corrosive behavior was due to a decrease in surface area. The literature does support that fluoride can corrode titanium alloys, but it does not support stress decreasing corrosion which our results showed. Although fluoride did appear to cause the greater effect on the corrosive behavior of the coils, clinically high levels of fluoride are short lived. Although fluoride may be introduced into the oral environment through drinking water, toothpaste, or fluoride treatments, the concentration quickly declines over time. On the other hand compression or stress on a coil is longer acting. If a NiTi coil is compressed between two teeth to create space, this stress is constant and can last over a month. If stress does actually affect the corrosive behavior of NiTi coils, clinically it would be more relevant than fluoride.

Keeping in mind that corrosion results in a release of ions from the metal, it is important to understand any adverse effects that may occur if these ions are released. Many orthodontic materials consist of some component of nickel, which can be released as an ion in the oral environment. Stainless steel, cobalt-chromium, and nickel-titanium are just a few examples of commonly used orthodontic alloys that contain nickel. Some alloys of nickel-titanium can contain up to 50% nickel. It has been found that 4.5 to 28.5% of the population have hypersensitivity to nickel, with a higher prevalence in females (Janson et al., 1998). Janson et al. studied nickel hypersensitivity reactions before, during, and after orthodontic treatment. When comparing the results of the three groups, they found that there was no significant difference in the prevalence of contact dermatitis. Kerosuo et al. (1996) performed a similar study of 700 adolescents and their results of a nickel allergy patch-test. The results showed that orthodontic treatment did not seem to affect the prevalence of nickel sensitization. Although nickel exposed to the oral environment may not illicit an allergic reaction, it has been asked why these allergens illicit this reaction extra-orally (Kerosuo et al., 1996). A study by Setcos et al. (2006) explained that oral mucosa is less reactive than skin. They go on to say that leachants from these materials may be swallowed before being absorbed in the mouth. The ability of a metal or alloy to induce and elicit allergic reactions appears to be related to the pattern and mode of corrosion. Mucosal allergies to metal may be rare due to the paucity of the stratum corneum on mucous membranes reduces the availability of carrier proteins to combine with metallic haptens to form complete antigens (Setcos et al., 2006). These reasons given may answer the question of why there is a difference between oral hypersensitivity compared to skin.

# CHAPTER 6
# CONCLUSION

The electrochemical properties of nickel-titanium coils in a stressed and unstressed state and immersed in artificial saliva and a fluoride solution were examined. Of the two factors under consideration, fluoride exhibited a greater effect than stress did, resulting in the coils having a lower open circuit potential and polarization resistance and a greater corrosion current. Since corrosion rate is proportional to ion release, more ions would be expected to be released from NiTi coils when exposed to fluoride.

# REFERENCES

Akid R. Corrosion of Engineering Materials. In *Handbook of Advanced Materials* (2004). Ed. Wessel JK. John Wiley & Sons, Inc.

Aksoy AU, Aras S. Use of nickel titanium coil springs for partially impacted second molars. J Clin Orthod. 1998 Aug;17(8):479-482. PubMed PMID: 985235

Angolkar PV, Arnold JV, Nanda RS, Duncanson MG Jr. Force degradation of closed coil springs: an in vitro evaluation. Am J Orthod Dentofacial Orthop. 1992 Aug;102(2):127-33. PubMed PMID: 1636629.

Binder RE. Easy placement of open-coil springs. J Clin Orthod. 2002 Nov; 36(11):626. PubMed PMID: 12638600.

Barlow M, Kula K. Factors influencing efficiency of sliding mechanics to close extraction space: a systematic review. Orthod Craniofac Res. 2008 May;11(2):65-73. PubMed PMID:18416747.

Barwart O. The effect of temperature change on the load value of Japanese NiTi coil springs in the superelastic range. Am J Orthod Dentofacial Orthop. 1996 Nov;110(5):553-8. PubMed PMID: 8922516.

Barwart O, Rollinger JM, Burger A. An evaluation of the transition temperature range of super-elastic orthodontic NiTi springs using differential scanning calorimetry. Eur J Orthod. 1999 Oct;21(5):497-502. PubMed PMID: 10565090.

Bokas J, Woods M. A clinical comparison between nickel titanium springs and elastomeric chains. Aust Orthod J. 2006 May;22(1):39-46. PubMed PMID: 16792244

Boshart BF, Currier GF, Nanda RS, Duncanson MG Jr. Load-deflection rate measurements of activated open and closed coil springs. Angle Orthod. 1990 Spring;60(1):27-32; discussion 33-4. PubMed PMID: 2316900.

Bourauel C, Drescher D, Ebling J, Broome D, Kanarachos A. Superelastic nickel titanium alloy retraction springs--an experimental investigation of force systems. Eur J Orthod. 1997 Oct;19(5):491-500. PubMed PMID: 9386335.

Bourke A, Daskalogiannakis J, Tompson B, Watson P. Force characteristics of nickel-titanium open-coil springs. Am J Orthod Dentofacial Orthop. 2010 Aug;138(2):142.e1-7; discussion 142-3. PubMed PMID: 20691352.

Brauchli LM, Senn C, Ball J, Wichelhaus A. Force levels of 23 nickel-titanium open-coil springs in compression testing. Am J Orthod Dentofacial Orthop. 2011 May;139(5):601-5. PubMed PMID: 21536202.

Carrillo R, Carillo RJ, Rossouw PE, Buschang PH. Closed-coil springs for intrusion mechanics with miniscrew anchorage. JCO. 2008 42(1): 17-18. PubMed PMID: 18296789.

Chaconas SJ, Caputo AA, Harvey K. Orthodontic force characteristics of open coil springs. Am J Orthod. 1984 Jun;85(6):494-7. PubMed PMID: 6587783

Eliades T, Bourauel C. Intraoral aging of orthodontic materials: the picture we miss and its clinical relevance. Am J Orthod Dentofacial Orthop. 2005 Apr;127(4):403-12. PubMed PMID: 15821684.

Erverdi N, Koyutürk O, Küçükkeles N. Nickel-titanium coil springs and repelling magnets: a comparison of two different intra-oral molar distalization techniques. Br J Orthod. 1997 Feb;24(1):47-53. PubMed PMID: 9088603.

Espinar-Escalona E, Llamas-Carreras JM, Barrera-Mora JM, Abalos-Lasbrucci C, Gil-Mur FJ. Effect of temperature on the orthodontic clinical applications of niti closed-coil springs. Med Oral Patol Oral Cir Bucal. 2013 May 31. [Epub ahead of print] PubMed PMID: 23722142.

Janson GR, Dainesi EA, Consolaro A, Woodside DG, de Freitas MR. Nickel hypersensitivity reaction before, during, and after orthodontic therap. Am J Orthod Dentofacial Orthop. 1998 Jun; 113(6):655-60. PubMed PMID: 9637569

Han S, Quick DC. Nickel-titanium spring properties in a simulated oral environment. Angle Orthod. 1993 Spring;63(1):67-72. PubMed PMID: 8507034.

Kerosuo H, Kullaa A, Kerosuo E, Kanerva L, Hensten-Petterson A. Nickel allergy in adolescents in relation to orthodontic treatment and piercing of ears. Am J Orthod Dentofacial Orthop. 1996 Feb;109(2):148-54. PubMed PMID: 8638560

Kumar YM, Ravindran NS, Balasubramaniam MR. Holographic analysis of the initial canine displacement produced by four different retraction springs. Angle Orthod. 2009 Mar;79(2):368-72. PubMed PMID: 19216610.

Liu JK, Lee TM, Liu IH. Effect of loading force on the dissolution behavior and surface properties of nickel-titanium orthodontic archwires in artificial saliva. Am J Orthod Dentofacial Orthop. 2011 Aug;140(2):166-76. PubMed PMID: 21803253

Maganzini AL, Wong AM, Ahmed MK. Forces of various nickel titanium closed coil springs. Angle Orthod. 2010 Jan;80(1):182-7. PubMed PMID: 19852659.

Manhartsberger C, Seidenbusch W. Force delivery of Ni-Ti coil springs. Am J Orthod Dentofacial Orthop. 1996 Jan;109(1):8-21. PubMed PMID: 8540487.

Melsen B, Topp LF, Melsen HM, Terp S. Force system developed from closed coil springs. Eur J Orthod. 1994 Dec;16(6):531-9. PubMed PMID: 7720798

Miura F, Mogi M, Ohura Y, Karibe M. The super-elastic Japanese NiTi alloy wire for use in orthodontics. Part III. Studies on the Japanese NiTi alloy coil springs. Am J Orthod Dentofacial Orthop. 1988 Aug;94(2):89-96. PubMed PMID: 3165245.

Nakagawa M, Matsuya S, Udoh K. Corrosion behavior of pure titanium and titanium alloys in fluoride-containing solutions. Dent Mater J. 2001 Dec;20(4):305-14. PubMed PMID: 11915624

Nattrass C, Ireland AJ, Sherriff M. An investigation into the placement of force delivery systems and the initial forces applied by clinicians during space closure. Br J Orthod. 1997 May;24(2):127-31. PubMed PMID: 9218110.

Nattrass C, Ireland AJ, Sherriff M. The effect of environmental factors on elastomeric chain and nickel titanium coil springs. Eur J Orthod. 1998 Apr;20(2):169-76. PubMed PMID: 9633170.

Nightingale C, Jones, SP. A clinical investigation of force delivery systems for orthodontic space closure. J Orthod. 2003 Sep;30(3):229-36. PubMed PMID: 14530421

Oztürk Y, Firatli S, Almaç L. An evaluation of intraoral molar distalization with nickel-titanium coil springs. Quintessence Int. 2005 Oct;36(9):731-5. PubMed PMID: 16163876.

Proffit WR, Fields HW, Sarver DM (2007). *Contemporary Orthodontics*. St. Louis, MO: Mosby Elsevier.

Reclaru L, Meyer JM. Effects of fluorides on titanium and other dental alloys in dentistry. Biomaterials. 1998 Jan-Feb;19(1-3):85-92. PubMed PMID: 9678854

Rozier RG, Adair S, Graham F, Iafolla T, Kingman A, Kohn W, Krol D, Levy S, Pollick H, Whitford G, Strock S, Frantsve-Hawley J, Aravamudhan K, Meyer DM. Evidence-based clinical recommendations on the prescription of dietary fluoride supplements for caries prevention: a report of the American Dental Association Council on Scientific Affairs. JADA. 2010 Dec;141(12):1480-9. PubMed PMID: 21158195

Rozman J, Mrvar P, Drevenšek M, Pečlin P. Evaluation of NiTi superelastic retraction coil springs for orthodontic tooth movement in rats. Biomed Mater Eng. 2010;20(6):339-48. PubMed PMID: 21263180.

Ryan A. Superelastic nickel titanium coil springs. British J Orthod. 1995 Nov;22(4):370-376. PubMed PMID: 8580107.

Samuels RH, Rudge SJ, Mair LH. A clinical study of space closure with nickel-titanium closed coil springs and an elastic module. Am J Orthod Dentofacial Orthop. 1998 Jul;114(1):73-9. PubMed PMID: 9674684.

Samuels RH, Rudge SJ, Mair LH. A comparison of the rate of space closure using a nickel-titanium spring and an elastic module: a clinical study. Am J Orthod Dentofacial Orthop. 1993 May;103(5):464-7. PubMed PMID: 8480716.

Santos AC, Tortamano A, Naccarato SR, Dominguez-Rodriguez GC, Vigorito JW. An in vitro comparison of the force decay generated by different commercially available elastomeric chains and NiTi closed coil springs. Braz Oral Res. 2007 Jan-Mar;21(1):51-7. PubMed PMID: 17384855.

Schiff N, Grosgogeat B, Lissac M, Dalard F. Influence of fluoride content and ph on the corrosion resistance of titanium and its alloys. Biomaterials. 2002 May;23(9):1995-2002. PubMed PMID: 11996041

Schneevoigt R, Bourauel C, Harzer W, Eckardt L. Biomechanical analysis of arch-guided molar distalization when employing superelastic NiTi coil springs. J Orofac Orthop. 1999;60(2):124-35. PubMed PMID: 10220980.

Schneevoigt R, Haase A, Eckardt VL, Harzer W, Bourauel C. Laboratory analysis of superelastic NiTi compression springs. Med Eng Phys. 1999 Mar;21(2):119-25. PubMed PMID: 10426512.

Setcos JC, Babaei-Mahani A, Silvio LD, Mjor IA, Wilson NH. The safety of nickel containing dental alloys. Dent Mater. 2006 Dec;22(12):1163-8. PubMed PMID: 16405986

Steinbach G, Armstrong D, Kharbanda O, Petocz P, Darendeliler M. An investigation of the forces used by clinicians to open spaces with coil springs. Aust Orthod J. 2006 Nov;22(2):115-20. PubMed PMID: 17203574.

Sonis AL. Comparison of NiTi coil springs vs. elastics in canine retraction. J Clin Orthod. 1994 May;28(5):293-5. PubMed PMID: 8613508

Suzuki A, Kanetaka H, Shimizu Y, Tomizuka R, Hosoda H, Miyazaki S, Okuno O, Igarashi K, Matini H. Orthodontic buccal tooth movement by nickel-free titanium-based shape memory and superelastic alloy wire. Angle Orthod. 2006 Nov;76(6):1041-6. PubMed PMID: 17090162

Tripolt H, Burstone CJ, Bantleon P, Manschiebel W. Force characteristics of nickel-titanium tension coil springs. Am J Orthod Dentofacial Orthop. 1999 May;115(5):498-507. PubMed PMID: 10229881.

U.S. Department of Health and Human Services Federal Panel on Community Water Fluoridation. U.S. Public Health Service Recommendation for Fluoride Concentration in Drinking Water for the Prevention of Dental Caries. Public Health Reports. 2015 July-August;130:1-14.

Vidoni G, Perinetti G, Antoniolli F, Castaldo A, Contardo L. Combined aging effects of strain and thermocycling on unload deflection modes of nickel-titanium closed-coil springs: an in-vitro comparative study. Am J Orthod Dentofacial Orthop. 2010 Oct;138(4):451-7. PubMed PMID: 20889050.

Von Fraunhofer JA, Bonds PW, Johnson BE. Force generation by orthodontic coil springs. Angle Orthod. 1993 Summer;63(2):145-8. PubMed PMID: 8498703.

Walker MP, White RJ, Kula KS. Effects of fluoride prophylactic agents on the mechanical properties of nickel-titanium-based orthodontic wires. Am J Orthod Dentofacial Orthop. 2005 Jun;127(6):662-9. PubMed PMID: 15953890

Webb RI, Caputo AA, Chaconas SJ. Orthodontic force production by closed coil springs. Am J Orthod. 1978 Oct;74(4):405-9. PubMed PMID: 281143.

Wichelhaus A, Brauchli L, Ball J, Mertmann M. Mechanical behavior and clinical application of nickel-titanium closed-coil springs under different stress levels and mechanical loading cycles. Am J Orthod Dentofacial Orthop. 2010 May;137(5):671-8. Erratum in: Am J Orthod Dentofacial Orthop. 2010 Dec;138(6):689. PubMed PMID: 20451787.

Weintraub J, Vig P, Brown C, Kowalski C. The prevalence of orthodontic extractions. Am J Orthod and Dentofacial Orthop. 1989 Dec; 96(6): 462-66. PubMed PMID: 2589256.

Yee JA, Türk T, Elekdağ-Türk S, Cheng LL, Darendeliler MA. Rate of tooth movement under heavy and light continuous orthodontic forces. Am J Orthod Dentofacial Orthop. 2009 Aug;136(2):150.e1-9; discussion 150-1. PubMed PMID: 19651334.

Yokoyama K, Ichikawa T, Murakami H, Miyamoto Y, Asaoka K. Fracture mechanisms of retrieved titanium screw thread in dental implant. Biomaterials. 2002 Jun;23(12):2459-65. PubMed PMID: 12033593

Yokoyama K, Kaneko K, Moriyama K, Asaoka K, Sakai J, Nagumo M. J Biomed Mater Res A. 2003 May 1;65(2):182-7 PubMed PMID: 12734810

Yokoyama K, Hamada K, Moriyama K, Aaoka K. Degradation and fracture of ni-ti superelastic wire in an oral cavity. Biomaterials. 2001 Aug;22(16):2257-62 PubMed PMID: 11456065