White Pigmented Atomic Layer Deposition Coatings on Orthodontic Archwires: Resistance to Sliding, Durability, and Corrosion

Rachel M. Yamakawa, DDS

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science in Orthodontics

Oregon Health & Science University
Portland, Oregon

December 2013

White Pigmented Atomic Layer Deposition Coatings on Orthodontic Archwires: Resistance to Sliding, Durability, and Corrosion

Rachel M. Yamakawa, DDS

Master of Science in Orthodontics Research Advisory Committee:

Signature: [redacted] Date: 12-19-13

Jack L. Ferracane, Ph.D.
Professor, Chair
Department of Restorative Dentistry
Oregon Health & Science University

Signature: [redacted] Date: 12-19-13

Professor
Director of Dental Research
Midwestern University

Signature: [redacted] Date: 12/17/13

David A. Covell, Jr., Ph.D., D.D.S.
Associate Professor, Chair
Department of Orthodontics
Oregon Health & Science University

Signature: [redacted] Date: 12/13/2013

Ana E. Castilla, D.D.S, M.S.
Assistant Professor
Department of Orthodontics
Oregon Health & Science University

Acknowledgements

Thank you to my thesis mentor, Dr. Jack Ferracane for advising me through the entire project and for all of your efforts and guidance.

Thank you to my thesis committee members, Dr. John Mitchell, Dr. David Covell, and Dr. Castilla for their support throughout the duration of this project.

Thank you to Dr. Harry Davis for the guidance and encouragement.

Thank you to Erica Robinson for her help with data collection.

Thank you to Opal Orthodontics for product donations.

Thank you to my co-residents, Jennifer Messenger, Megan Miller, and David Moradi for their friendship and advice.

Thank you to Toby for his love and encouragement.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

White Pigmented Atomic Layer Deposition Coatings on Orthodontic Archwires: Resistance to Sliding, Durability, and Corrosion

Rachel M. Yamakawa, DDS[a], Harry Davis, PhD[b], Sean W. Smith, MS[c], John F. Conley, PhD[c], John C. Mitchell, PhD[d], David A. Covell, DDS, PhD[a], Jack L. Ferracane, PhD[c]

[a] Department of Orthodontics, School of Dentistry, Oregon Health & Science University, Portland, OR

[b] Department of Restorative Dentistry, Division of Biomaterials and Biomechanics, School of Dentistry, Oregon Health & Science University, Portland, OR

[c] School of Electrical Engineering and Computer Science, Oregon State University, Corvallis, OR

[d] Department of Dental Research, College of Dental Medicine, Midwestern University, Glendale, AZ

Keywords: dental esthetics, coating, resistance to sliding, atomic layer deposition, corrosion

Corresponding Author:

Jack L. Ferracane, PhD
Professor, Chair
Department of Restorative Dentistry
Oregon Health & Science University
School of Dentistry
611 SW Campus Drive
Portland, OR 97239
Phone: 503-494-4327
Fax: 503-494-5777
ferracan@ohsu.edu

White Pigmented Atomic Layer Deposition Coatings on Orthodontic Archwires: Resistance to Sliding, Durability, and Corrosion

ABSTRACT

Objective: To test the resistance to sliding, durability, and corrosion of stainless steel archwires coated with white pigment and atomic layer deposition (ALD).

Materials and Methods: White pigmented ALD coated archwires were tested along with ALD archwires and as-received archwires. A bracket was ligated and pulled parallel to the archwire and force measurements recorded over 5 cm to determine the resistance to sliding. The durability of the coatings was tested by measuring the amount of mass lost following placement of three 0.75 mm second-order step bends in each wire. The ion release from the wires soaked in an acid solution following the resistance to sliding test and from wires not exposed to sliding was determined by inductively coupled plasma mass spectroscopy analysis (ICP-MS). Data was analyzed using ANOVA/ Tukey's ($p<0.05$).

Results: The white pigmented ALD coated wire that received two coats of both pigment and ALD had the highest resistance to sliding while the as-received wire had the lowest. The white pigmented ALD two-coat wire had the greatest change in mass following placement of the step bends. The ALD wire that was not slid had the lowest levels of chromium, manganese, iron, and nickel compared to all other wire types but was not significantly different from the as-received wire. There were significantly higher levels of aluminum detected for ALD, white pigmented ALD one-coat, and white pigmented ALD two-coat wires as compared to as-received wires. There were significantly higher levels of manganese, iron, and nickel released for the white pigmented ALD one-coat and two-coat wires. The white pigmented wires that were subjected to sliding had significantly higher levels of aluminum and titanium released compared to wires that

were not subjected to sliding. The white pigmented ALD two-coat wire that was slid had the highest values of released titanium, iron, nickel, and copper.

Conclusions: ALD coatings increased the resistance to sliding. The data show trends towards the ALD wires having improved corrosion resistance compared to as-received wires. The addition of the white pigment further increased the resistance to sliding and caused an increase in the ion release from the pigmented ALD layer. The action of the bracket sliding on the archwire affected the ion release. Following placement of the step bends the extent of the damage to the coating of white pigmented ALD wires was limited to the areas where the step plier was applied.

INTRODUCTION

With the increasing demand for esthetic orthodontic treatment, much progress has been made in the development of clear brackets for use in labial orthodontics (Russell 2005). However the most effective wires continue to be fabricated from non-esthetic metal alloys due to superior mechanical properties, flexibility, strength, and chemical resistance (Burstone et al. 2011, Silva et al. 2013a). With the metal wires clearly visible, the esthetic appearance is not optimal and can be unacceptable for the esthetically concerned patient.

To maintain mechanical properties and improve esthetics, metallic archwires have been coated with tooth-colored polymers or inorganic materials. Materials used in the coating are often polytetraflouroethlyene (Teflon) or low reflectivity rhodium (Bradley et al. 2013). However, many lack translucency and in some cases the outer coating can wear or peel, leading to large surface defects and accumulation of the coating in the bracket edges (Neumann et al. 2002). Polymeric wires made of a self-reinforced polymer composite, polyphenylene, are translucent but experience stress relaxation over time (Burstone et al. 2011). Currently coated alloy wires are the only esthetic archwires available for use (Aksakalli et al. 2013).

Atomic Layer Deposition (ALD) coatings on orthodontic archwires have shown positive results with lower resistance to sliding and lower coefficient of friction compared to uncoated controls (Werner et al. 2011). ALD is a chemical gas phase thin film deposition technique that deposits a highly uniform coating with film thickness control. The method involves exposing the archwire to gaseous precursors in a cyclic manner, growing a thin uniform coating of a desired thickness that is covalently bound to the underlying surface (Ritala et al. 2001). While the ALD coating is transparent rather than tooth-colored, it can be used to protect and insulate particles to prevent particle oxidation and modify mechanical properties (George 2010).

The use of coatings also can be used to help prevent the corrosion of orthodontic archwires in the oral environment. Teflon coatings tested in-vitro suppressed the corrosion process completely while ion implantation only slightly reduced the amount of corrosive destruction (Neumann et al. 2002). Corrosion is an electrochemical process that results from the loss of metal ions directly into solution or due to the progressive dissolution of a surface film (House et al. 2008). Most orthodontic appliances are made from a stainless steel alloy including nickel, chromium, cobalt, iron, molybdenum, and titanium (Regis Jr et al. 2011). The continuous exposure to saliva and acidic conditions can accelerate the corrosion process. The major corrosion products for stainless steel are iron, chromium, and nickel. Nickel sensitivity is a concern in the dental profession and nickel has been shown to have carcinogenic, mutagenic, and cytotoxic effects (House et al. 2008).

There is little information in the literature on the corrosion of the ALD coatings and no studies have been conducted to examine esthetic ALD coated stainless steel archwires. Therefore the aims of this research were to evaluate the frictional behavior, durability, and corrosion of esthetic ALD coatings on stainless steel archwires compared with as-received stainless steel wires from the manufacturers.

MATERIALS AND METHODS

Straight stainless steel wire with a size of 0.019" x 0.025" (G & H Orthodontics, Franklin, IN) and stainless steel upper premolar brackets with a slot dimension of 0.022" x 0.028" with -7° torque and 0° angulation (Avex MX, Opal Orthodontics, South Jordan, UT) were provided by the manufacturer from their commercial supply.

ALD Coating and Pigmenting Process

A total of 80 stainless steel wires (cut to a length of 19 cm) and 60 brackets were randomly selected. To remove potential surface contaminants, the wires and brackets were ultrasonically cleaned using in sequence of acetone, isopropyl alcohol, and deionized water before being dried in an oven for 5 minutes at 130°C.

Forty of the wires were randomly selected to receive the white coating composed of aluminum oxide and titanium dioxide particles in a spray-on paint (Rustoleum, Vernon Hills, IL). The coating was selected due to the fine particle size and expected biocompatibility of the oxides. The initial intent was to apply enough coating to make the wire uniformly white. However it was apparent that with such a large thickness of a uniform layer of coating, the ALD was unable to penetrate the coating to bond to the surface of the wire, causing the pigment to easily flake off. Therefore one non-uniform layer of white pigment was sprayed onto each of the four surfaces of the wire by placing the wire on a lathe and applying the coating through mesh gauze (5 cm x 20 cm) to omit larger pigment particles while turning the wire to expose all surfaces. The painted wires were placed in an oven for 30 minutes at 315°C to remove the organic binder in the paint, leaving only the particles. The wire was subsequently plasma cleaned (Plasma Etch, Carson City, NV) to remove any residual organic substances from the pigment.

All 40 wires underwent the ALD thermal process in addition to 20 as-received controls. The ALD process was performed in an Arradiance Gemstar 6 atomic layer deposition unit (Sudbury, MA). Wires were supported at the ends to allow uniform deposition along the central region of the wire. Twenty pigmented wires received a coating of 136 nm Al_2O_3, while twenty pigmented wires received a coating of 249 nm Al_2O_3 (white pigmented ALD one-coat wires) by reaction of Trimethylaluminum (TMA) and water at 175°C.

In an effort to improve the esthetics of the white pigmented ALD one-coat wire, the wires that received 136 nm Al_2O_3 then had a second layer of white pigment deposited following the same protocol to apply the first layer. The wires were again placed in the oven for 30 minutes at 315°C and plasma cleaned before receiving a final 249 nm Al_2O_3 (white pigmented ALD two-coat wires). Silicon wafers were placed alongside the wires to measure the coating thickness by ellipsometry.

Resistance to Sliding

Fifteen white pigmented ALD one-coat wires, 15 white pigmented ALD two-coat wires, 15 ALD wires, and 15 as-received wires (length 19 cm) were tested along with 60 as-received brackets. A custom-fabricated friction-testing device, based on that described by Werner et al. (2011) was used to record the force necessary to move the bracket along the wire (Figure 3). The lower end of the test unit was attached to a heavy base block on the lower support of the testing machine. The upper attachment had a soldered wire attached to a free-spinning washer around the load cell attached to the movable crosshead. This configuration allowed the upper attachment to freely spin and eliminated the introduction of torque between the wire and bracket.

The bracket was ligated to the wire with gray elastomeric ligatures (3M Unitek, Monrovia, CA) 50 mm from the end of the wire. The wire was inserted into the lower attachment and clamped tightly to ensure stability. The .018" stainless steel wire was attached to the bracket base in a passive configuration.

Testing was performed on a MTS Q Test (MTS Systems, Eden Prairie, MN) with a crosshead speed of 5 mm/min over a 5 cm span. The bracket was pulled with a force parallel to the wire. All testing was done by the same operator. Data was plotted as a load versus distance traveled curve. The area under the graph was measured using Image J software (W. Rasband, National Institutes of Health, Bethesda, MD). The amount of work (g x mm) required for each wire to be slid 5 cm was calculated with the following equation: (pixels under the curve/pixels of total plot area) x total area in g x mm.

Durability of the white pigmented ALD coating

Five of each of the four wire types: white pigmented ALD one-coat wires, white pigmented ALD two-coat wires, ALD wires, and as-received wires were weighed twice (Mettler Instrument Corp, Hightstown, NJ) to determine the initial mass of each wire. Three 0.75 mm bends placed approximately 1 cm apart were placed in each wire using a 0.75 mm step plier (Orthopli, Philadelphia, PA) to replicate clinical conditions of second-order finishing bends placed in an archwire. Following the placement of the step bends, compressed air was blown on the wire to remove any loose debris or coating. Each wire was then weighed twice and the amount of mass loss calculated for each wire to determine the durability of the adhesion of the coating to the wire.

Ion Release

Ion release from the four types of wires was measured to test the corrosion potential of the coating/wire combination. The solution was comprised of 90% lactic acid ($C_3H_6O_6$), sodium chloride (NaCl), deionized water (H_2O), and ethanol (C_2H_6O) with a pH of 2.3 +/- 0.1 based on the American Dental Association Specification Number 97 Corrosion Test Methods. A 4.5 cm portion of the wire that had been slid during the resistance to sliding test was taken from five wires for each of the four wire types and placed in 3.5 ml of corrosion solution at 37°C for 7 days +/-1 hr to test whether the action of sliding the bracket along the wire affected the corrosion potential of the coating or wire. In addition, five unslid white pigmented ALD one-coat wires, white pigmented ALD two-coat wires, ALD wires, and as-received wires were cut to the same length and placed in 3.5 ml of corrosion solution at 37°C. The wires were removed after 7 days +/-1 hr and rinsed with deionized water. For ion content analysis, 1 ml of each solution was stored at room temperature for inductively coupled plasma mass spectroscopy analysis (ICP-MS; Agilent 7700x, Santa Clara, CA). Each sample was measured in triplicate with the instrument detection limit of 0.0218 ppb for aluminum, 0.0398 ppb for titanium, 0.0061 ppb for chromium, 0.0203 ppb for manganese, 0.0403 ppb for iron, 0.0070 ppb for nickel, and 0.0103 ppb for copper.

Statistical Analysis

The work of sliding for the as-received, ALD, and white pigmented ALD wires were analyzed using a one-way analysis of variance. A Tukey post-hoc test was used to identify intragroup differences. A one-way analysis of variance and a Tukey post-hoc test were used to analyze the mass loss for the four wire types. The ion release results of each group were submitted to a two-way analysis of variance test and Tukey post-hoc test to verify the effect of sliding and the ion release and the interaction of both factors on the results. All statistics were performed at a 5% level of significance.

To determine the measurement error for the work of sliding, four load versus distance traveled graphs were randomly selected and re-measured using Image J software (W. Rasband, National Institutes of Health, Bethesda, MD).

RESULTS

Resistance to Sliding

Results of the comparisons between the four groups are shown in Figure 4. The ANOVA revealed significant differences between all four groups ($p< 0.05$). The as-received wire required the least amount of work and had the lowest resistance to sliding, followed in increasing order by the ALD wire, white pigmented ALD one-coat wire, and white pigmented ALD two-coat wire. The white pigmented ALD two-coat wire required the greatest amount of work and had the highest resistance to sliding.

Durability of the white pigmented ALD coating

Figure 5 shows significant differences between the as-received and white pigmented ALD one-coat and the as-received and white pigmented ALD two-coat wires ($p<0.05$). No significant differences in mass loss for the as-received and ALD wire ($p=0.133$), white pigmented ALD one-coat and white pigmented ALD two-coat wire ($p=0.054$), and ALD and white pigmented ALD one-coat wire ($p=0.705$) were observed. The white pigmented ALD two-coat wire had a significantly greater loss in mass than the as-received wire ($p<0.001$).

Ion Release

The results from the corrosion test (Table 1) showed there was not a significant difference in the level of chromium ($p=0.993$), manganese ($p=1.000$), iron ($p=0.973$), and nickel ($p=1.000$) released between the ALD wire and the as-received wire. There were significantly higher levels of aluminum released for ALD, white pigmented ALD one-coat and two-coat wires as compared to as-received wires ($p<0.05$). However there was no significant difference in released aluminum ($p=0.183$) between pigmented ALD one-coat and two coat wires.

There were significantly higher levels of manganese, iron, and nickel released for the white pigmented ALD one-coat and two-coat wires as compared to as-received wires ($p<0.05$). The white pigmented ALD one-coat and two-coat wires that were slid had significantly higher levels of aluminum and titanium released compared to unslid wires ($p<0.05$). The white pigmented ALD two-coat wire that was slid had the highest release of titanium, iron, nickel, and copper. However the level of copper was not statistically significant ($p=0.236$).

DISCUSSION

An ideal coating on an archwire would be esthetic and maintain the same mechanical properties of a stainless steel wire with a decreased resistance to sliding. While different types of tooth colored coatings have been used to improve esthetics, many have unwanted side effects. Some studies have reported a decrease in friction of coated archwires compared to non-coated archwires (Aksakalli et al. 2013). However others have described coatings as not durable with damage from mastication forces and delamination of the coating from the underlying metal during usage in the oral cavity (Elayyan et al. 2008).

The surface quality of the archwire affects the area of surface contact and can influence the effectiveness of tooth movement (Silva et al. 2013b). There is conflicting evidence between surface roughness and frictional force. Kusy and Whitley (1990) stated that although the surface roughness of different wires showed a positive correlation with their coefficient of friction, frictional loss and the rate of orthodontic tooth movement is a complex multifactorial process. In contrast, Doshi and Bhad Patil (2011) found there was no correlation between the wire roughness and frictional resistance.

Various coatings such as Teflon, ion implantation, and diamond-like carbon coating have been shown to reduce the resistance to sliding by affecting the surface of the archwire (Farronato et al. 2011). Studies on esthetic coated archwires have found that a plastic coating decreased friction between archwires and brackets, while others have found the coated surfaces to be rougher than those of corresponding noncoated wires but sliding friction was not tested (Husmann et al. 2002, Iijima et al. 2012).

Our study showed the pigmented ALD coatings increased the resistance to sliding as compared to as-received wires. The white pigmented ALD two-coat wire had the greatest resistance to sliding followed by the pigmented ALD one-coat wire, ALD wire, and as-received wire. Some studies on esthetic wires have found the external surface had a significantly lower hardness and elastic modulus than noncoated wires and concluded that the coating layers might influence their frictional characteristics (Iijima et al. 2012). Silva et al. (2013b) found that as-received wires did not show a uniform coating thickness, with wires having a thicker coating in the center and thinner coating on the edges of the labial surface. In the current study, the white pigmented wires had a single, non-uniform layer of white pigment to allow the ALD direct access to the wire to establish adhesion. However, the pigmenting process resulted in an uneven deposition of pigment particles and tendency for the particles to clump together (Figure 2). This prevented a smooth surface of ALD coated pigment on the wire and may have contributed to an increased overall roughness and resistance to sliding.

The resistance to sliding could also have been influenced by the increased dimension of the wire from the addition of the white coating and ALD. A wire with a smaller cross section will help to facilitate the initiation of sliding mechanics and lead to a decrease in frictional forces (Kusy and Whitley 1999). The thickness of one layer of coating in this study was around 10 μm, while most coatings are approximately 50.80 μm in thickness (Aksakalli et al. 2013). In this study the white pigment was applied to all four surfaces of the wire. To account for the thickness of the coating layer, manufacturers of some esthetic wires decrease the inner alloy core dimensions. However due to the smaller size of the stainless steel core, such wires are expected to have a different mechanical behavior than an uncoated wire with the same dimension (Silva et al. 2013a). Another solution to producing an esthetic wire with enhanced sliding mechanics could be to provide a coating layer only on the labial surface of the wire that would not contact the bracket and minimize any interference from the coating during sliding (Silva et al. 2013a).

While the addition of the white pigment increased the resistance to sliding, the difference between the as-received wire and the white pigmented ALD one-coat wire was similar to other wire types. Juvvadi et al. (2010) compared three types of straight wires and found that titanium-molybdenum alloy (TMA) wires had the highest frictional force value while stainless steel wires showed the lowest values. The TMA wire showed a 30% increase in static friction and 33% increase in kinetic friction compared to the stainless steel wire. Similarly Doshi and Bhad-Patil (2011) found the stainless steel bracket and TMA wire had a 42.86% increase in the frictional resistance compared to the stainless steel bracket and wire couple. The current study showed about a 76% increase in the resistance to sliding between the as-received wire and the white pigmented ALD one-coat wire with an equivalent bracket.

The ALD wire also showed a higher resistance to sliding than the as-received wire. In contrast, Werner et al. showed a decrease in the resistance to sliding with the ALD coating as compared to as-received wires due to a higher hardness and reduction in the coefficient of friction (2011). Such a difference may be due to the increased thickness of the ALD layer used in this study. Another cause could be differences in batches of wires and brackets, as other studies have found that variations in the frictional resistances ranged up to 2.5 times among brackets of the same brand (Regis et al. 2011).

An esthetic archwire will only remain esthetic if the white coating is able to withstand the mechanical forces found in the oral environment. A previous study by Neumann et al. demonstrated the delamination of certain areas of Teflon coating following cyclic mechanical loading tests (Neumann et al. 2002). In vivo, an average of 25 percent of the coating was lost within 33 days, exposing the metallic surface below (Elayyan et al. 2008). The coating was primarily lost where it was engaged in the bracket with less damage in the inter-bracket span

(Bradley et al. 2013). Delamination can have an impact on friction as the surface defects on the wire contact the edges of the brackets and may impede archwire sliding (Bradley et al. 2013). In addition, the irregular surfaces found microscopically may lead to plaque accumulation in the wire surface defects, further reducing the sliding properties of the archwire (Elayyan et al. 2008, Neumann et al. 2002).

Bradley et al. (2013) surveyed patients who had been treated using coated wires and found that half of the patients were aware of color and texture changes over time, with patient satisfaction decreasing significantly as the coating was lost in the mouth. Studies have found that the peeling started at the upper and lower labial edges and then moved toward the center of the surface (Silva et al. 2013b).

No studies have mentioned the ability of esthetic stainless steel wire coatings to withstand adjustment bends commonly placed in the wire during the detailing and finishing stages of orthodontic treatment. Manufacturers of esthetic wires state the wires can accept first, second, and third order bends but there is little research to demonstrate the effect of such bends on the coating (www.orthoorganizers.com). It is evident from the images of the four wires (Figure 6) that the pigmented ALD wires lost some of the coating in the area where the step plier was applied. However, there was only a 0.015% change in weight loss for the white pigmented ALD one-coat wire and a 0.028% loss for the white pigmented ALD two-coat wire. While there was a visible loss of coating for both the one-coat and two-coat white pigmented ALD wires, the extent of the damage to the coating was limited to the areas where the step plier was placed on the wire. The step bend did not cause visible delamination of the coating from the adjacent wire segments.

There was not a statistical difference in weight loss between the pigmented ALD one-coat and pigmented ALD two-coat wires. The addition of the second layer of pigment and ALD did not appear to greatly change the adherence of the coating to the underlying wire and suggests the possibility of adding further layers of white coating to create an even more esthetic wire with a durable coating. Furthermore, this suggests the clinical application of using the wire for first, second, and third order bends without significantly compromising the esthetics of the coating. However, more research is needed to prove this hypothesis.

While the ALD wire did visibly appear to lose some of the coating, there was not a significant difference in mass loss between the as-received and ALD wire. Werner et al. (2011) determined that the ALD coating did not delaminate from the wire after nanomechanical scratch testing. This difference was likely due to different test methods. Our study tried to replicate the clinical conditions of finishing bends that would place the wire and coating under both compressive and tensile forces upon use of an orthodontic plier.

According to the manufacturer, stainless steel Opal brackets are composed of iron, chromium, nickel, and copper (www.opalorthodontics.com). The manufacturer of stainless steel G & H Orthodontic wire lists the following composition: iron, chromium, nickel, manganese, cobalt, and trace elements of silicon, carbon, phosphorus, and sulfur (www.ghwire.com). Because the ALD coating has aluminum oxide and the white pigment contained titanium dioxide, the four wire types were tested for the release of aluminum, titanium, chromium, manganese, iron, nickel, and copper, and analyzed simultaneously by inductively coupled plasma mass spectroscopy. ICP-MS was selected because of its sensitivity and ability to detect variations in ion concentration in the range of parts per billion.

The degradation of orthodontic appliances in the oral environment is influenced by many factors. Pitting and crevice corrosion can form on the surface of as-received orthodontic wires and brackets due to the fact that the wires are not perfectly smooth. Microscopically there are many pits and crevices that can increase the susceptibility to corrosion because of their ability to harbor plaque-forming microorganisms (House et al. 2008). Neumann et al. (2002) found that corrosion defects occurred predominantly at the edges of the wires in the shape of large pits. Other studies have shown that surface residual stress produced during the manufacturing process might be more important than surface roughness in the susceptibility of wires to corrosion (House et al. 2008).

Various authors have tested the corrosion resistance of coated wires. Kim and Johnson (1999) found that nitride coatings did not affect corrosion whereas the epoxy coating predictably improved corrosion resistance. Another study determined that the extent of surface destruction was reduced by ion implantation (Neumann et al. 2002). The current study did not show a significant effect of ALD on corrosion resistance, but there were trends toward the unslid ALD wire releasing lower values of chromium, manganese, iron, and nickel compared to the as-received wire. The decrease in the release of such ions could demonstrate the ability of ALD to improve the corrosion resistance. The nonsignificant finding could be due to the large variation in ion release and small sample size (n=5 for each group). The slid ALD wire had higher levels of chromium, manganese, iron, and nickel than the slid as-received wire, but the difference was not significant.

While there was a decrease in the amount of released chromium, manganese, iron, and nickel for the ALD wire, there was a significantly higher level of aluminum detected for the

ALD wire as compared to the as-received wire. This indicates the protective effect of ALD but also demonstrates the dissolution of the ALD coating in the acidic solution.

The addition of the pigment layer did not improve the corrosion resistance. There were significantly higher levels of manganese, iron, and nickel for white pigmented ALD wires as compared to as-received wires. This may be due to heating during the pigmenting process that caused the diffusion of atoms from the wire into the pigment layer. In addition, there were significantly higher levels of aluminum detected for the white pigmented ALD wires as compared to as-received and ALD wires. The uneven deposition of the pigment particles may have resulted in an increased surface area of the white pigmented ALD wires and contributed to the increased ion release. Krishnan et al. (2013) stated that the type of coating material rather than the surface roughness played a critical role in expressing anticorrosive features. In contrast, Neumann et al. (2002) found that there was no direct connection between the material of the coating and the corrosion resistance.

The results of this study also demonstrate the action of the bracket sliding on the archwire had an effect on the ion release. Aluminum is the major component of both the ALD coating and white pigment, while titanium is a component of the white pigment. The ALD, white pigmented ALD one-coat and two-coat wires that were slid showed a significantly higher release of aluminum as compared to wires that were not slid. Furthermore, both white pigmented ALD one-coat and two-coat wires that were slid showed a significant increase in the level of titanium released compared to unslid wires. When an archwire is ligated to an orthodontic bracket, the reactivity of the metal alloy increases at the sites of stress and stress corrosion can occur (House et al. 2008). Neumann et al. (2002) found that once the coating was affected during mechanical tests it allowed the corrosion process to start at those regions. He found that Teflon coatings suppressed corrosion processes completely but following surface defects and a certain interval of time the corrosion behavior of the core wire overcame the protective effect of the Teflon coating.

Figure 7 shows the labial surface of a white pigmented ALD one-coat wire that was not touching the bracket sides compared to the underside of the wire adjacent to the bracket. The surfaces of both the white pigmented ALD one-coat and two-coat wires that were slid showed areas of metallic debris on the side of the wire adjacent to the bracket, with no obvious signs of delamination. The white pigmented ALD two-coat wire that was slid had the highest release of titanium, iron, nickel, and copper compared to all wire types. While the difference in copper between slid and unslid wires was not significant, copper is primarily found in the bracket. Therefore it is possible that the metallic areas are deposits of metal from the wear of the bracket during sliding. In addition, the ALD, white pigmented ALD one-coat, and white pigmented ALD two-coat wires that were slid all had higher trends of increased copper release compared to wires that were not slid. Iron and nickel are found in both the bracket and wire composition. Thus it is possible that the increased iron and nickel detected were from the degradation of the bracket as well as from the diffusion of atoms from the wire into the pigment layer.

The white pigmented ALD one-coat wire that was not slid released a significantly higher amount of chromium, manganese, iron, and nickel than the wire that was slid. This somewhat anomalous result may be due to the large variation in ion release and small sample size (n=5 for each group).

CONCLUSIONS

ALD coatings resulted in an increase in the resistance to sliding, but trended toward improved corrosion resistance compared to as-received wires. The addition of the white pigment prior to ALD coating enhanced the esthetic aspects of the wire, but further increased the resistance to sliding, likely due to the increase in wire size dimension and surface roughness of the non-uniform coating. While the white pigmented ALD two-coat wire had the greatest amount of mass loss following placement of the second-order finishing bends, the extent of the damage to the coating was limited to the areas where the step plier was applied, suggesting that the pigment/coating combination was relatively durable. There were significantly higher values of manganese, iron, and nickel release detected for the white pigmented ALD wires compared to ALD and as-received wires, possibly due to the heating process causing the diffusion of atoms from the wire into the pigment layer. The action of the bracket sliding on the archwire increased the amount of aluminum released for the ALD, white pigmented ALD one-coat and white pigmented ALD two-coat wires.

With the increasing trend for esthetic orthodontic treatment, the demand for esthetic archwires will only continue to rise. Future studies are needed to compare the mechanical properties, durability, and corrosion potential of esthetic archwires on the market to allow the clinician to understand the limitations of the wire and make the best choice for the patient.

REFERENCES

1. Russell JS. Aesthetic orthodontic brackets. J Orthod 2005;32:146-63.
2. Burstone CJ, Liebler SAH, Goldberg AJ. Polyphenylene polymers as esthetic orthodontic archwires. Am J Dentofacial Orthop. 2011;139:e391-e398.
3. Silva DLA, Mattos CT, Sant' Anna EF, Ruellas ACDO, Elias CN. Cross-section dimensions and mechanical properties of esthetic orthodontic coated archwires. Am J Orthod Dentofacial Orthop. 2013;143:S85-S91.
4. Bradley TG, Berzins DW, Valeri N, Pruszynski J, Eliades T, Katsaros C. An investigation into the mechanical and aesthetic properties of new generation coated nickel-titanium wires in the as-received state and after clinical use. Eur J Orthod. 2013;10:1-7.
5. Neumann P, Bourauel C, Jager A. Corrosion and permanent fracture resistance of coated and conventional orthodontic wires. J Mater Sci Med. 2002;13:141-147.
6. Aksakalli S, Malkoc S. Esthetic orthodontic archwires: Literature review. J Orthod Res. 2013;1:2-4.
7. Werner G, Smith S, Conley J, Mitchell JC. Atomic Layer Deposition Coated Orthodontic Archwires to Reduce Coefficient of Friction. MS thesis 2011.
8. Ritala M, Leskela M. Handbook of Thin Film Materials. Chapter 2: Atomic Layer Deposition. 2001;103-155.
9. George, SM. Atomic Layer Deposition: An Overview. Chem Rev. 2010;110:111-131.
10. House K, Sernetz F, Dymock D, Sandy JR, Ireland AJ. Corrosion of orthodontic appliances—should we care? Am J Orthod Dentofacial Orthop. 2008;133:584-592.

11. Regis Jr, S. Soares P, Camargo ES, Filho OG, Tanaka O, Maruo H. Biodegradation of orthodontic metallic brackets and associated implications for friction. Am J Orthod Dentofacial Orthop. 2011;140:501-509.

12. Elyyan F, Silikas N, Bearn D. Ex vivo surface and mechanical properties of coated orthodontic archwires. Eur J Orthod. 2008; 30:661-67.

13. Silva DLA, Mattos CT, Simao RA, Ruellas ACO. Coating stability and surface characteristics of esthetic orthodontic coated archwires. Angle Orthod. In-Press. 2013.

14. Kusy RP, Whitley JQ. Effects of surface roughness on the coefficients of friction in model orthodontic systems. J Biomechanics. 1990; 23: 913-25.

15. Doshi UH, Bhad-Patil WA. Static frictional force and surface roughness of various bracket and wire combinations. Am J Orthod Dentofacial Orthop. 2011;139:74-79.

16. Farronato G, Maijer R, Caria MP, Esposito L, Alberzoni D, Cacciatore G. The effect of Teflon coating on the resistance to sliding of orthodontic archwires. Eur J Orthod. 2011;10:1-8.

17. Husmann P, Bourauel C, Wessinger M, Jager A. The frictional behavior of coated guiding archwires. J Orofac Orthop. 2002;63:199-211.

18. Iijima M, Muguruma T, Brantley WA, Choe HC, Nakagaki S, Alapati SB, Mizoguchi I. Effect of coating on properties of esthetic orthodontic nickel-titanium wires. Angle Orthod. 2012;82:319-325.

19. Kusy RP, Whitley JQ. Influence of archwire and bracket dimensions on sliding mechanics: derivations and determinations of the critical contact angles for binding. Eur J Orthod. 1999;21:199-207.

20. Juvvadi SR, Kailasam V, Padmanabhan S, Chitharanjan AB. Physical, mechanical, and flexural properties of 3 orthodontic wires: An in-vitro study. Am J Orthod Dentofacial Orthop. 2010;138:623-630.

21. www.orthoorganizers.com

22. www.opalorthodontics.com

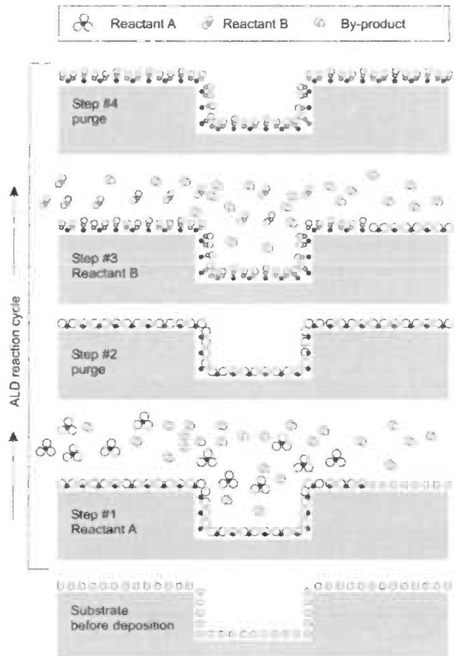
23. www.ghwire.com

24. Kim H, Johnson JW. Corrosion of stainless steel, nickel-titanium, coated nickel-titanium, and titanium orthodontic wires. Angle Orthod. 1999;69:39-44.

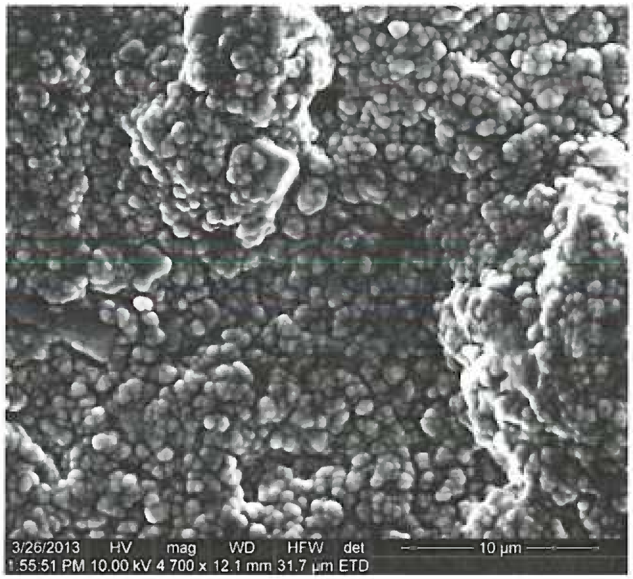
25. Krishnan M, Seema S, Kumar AV, Varthini NP, Sukumaran K, Pawar VR, Arora V. Corrosion resisance of surface modified nickel titanium archwires. Angle Orthod. In-Press. 2013.

26. Puurunen RL. Surface chemistry of atomic layer deposition: A case study for the trimethylaluminum/water process. J App Physics. 97;121301-1-121301-50.

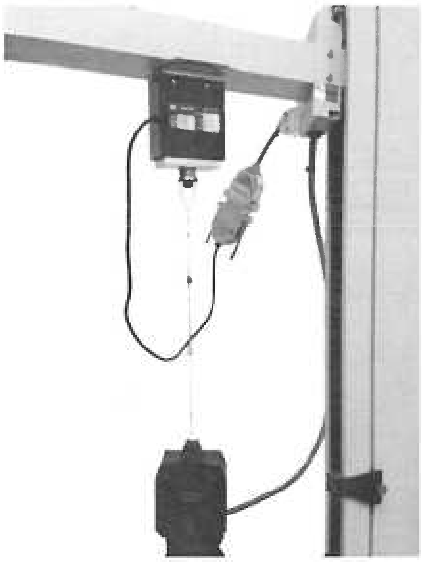
LIST OF FIGURES

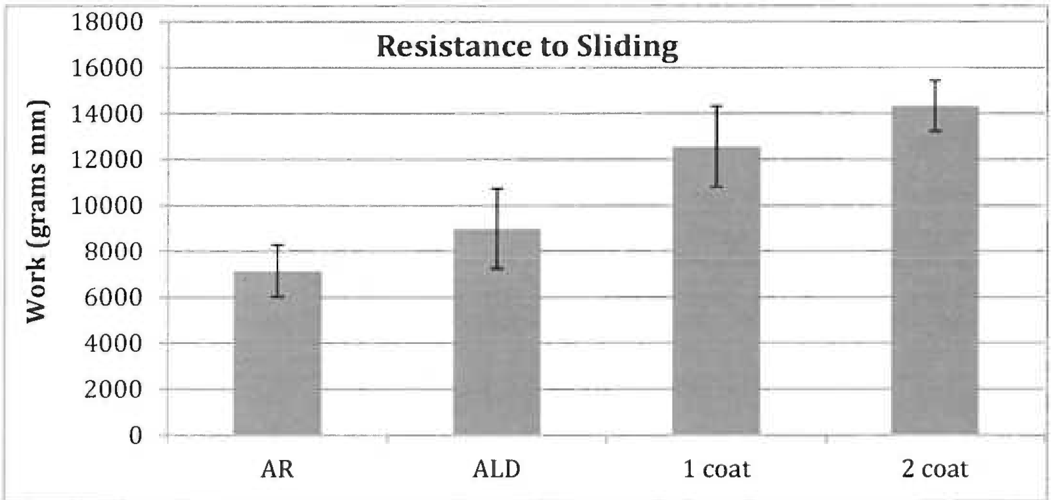


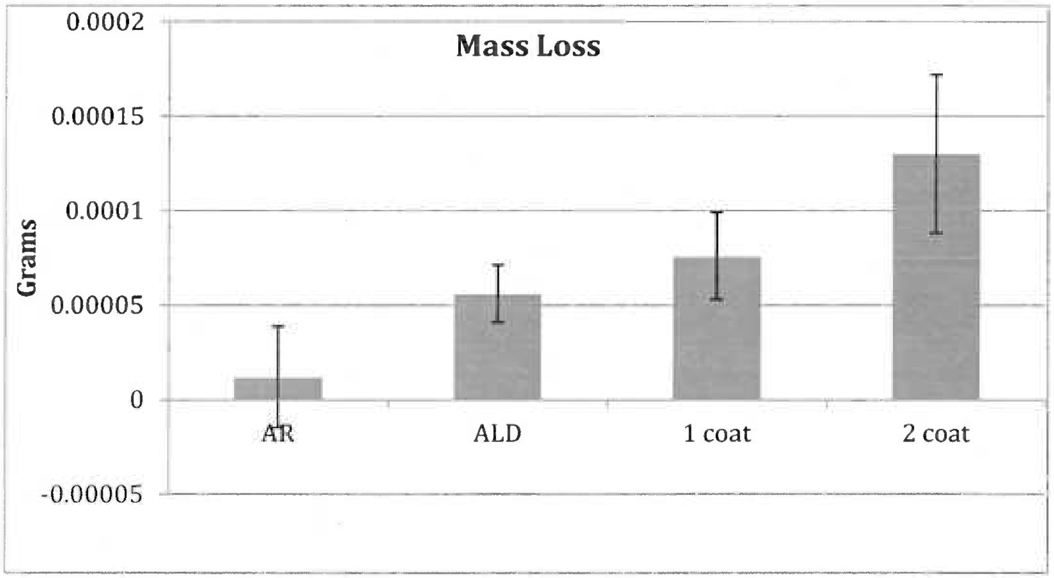
Puurunen RL. Surface chemistry of atomic layer deposition: A case study for the trimethylaluminum/water process. J App Physics. 97;121301-1-121301-50.



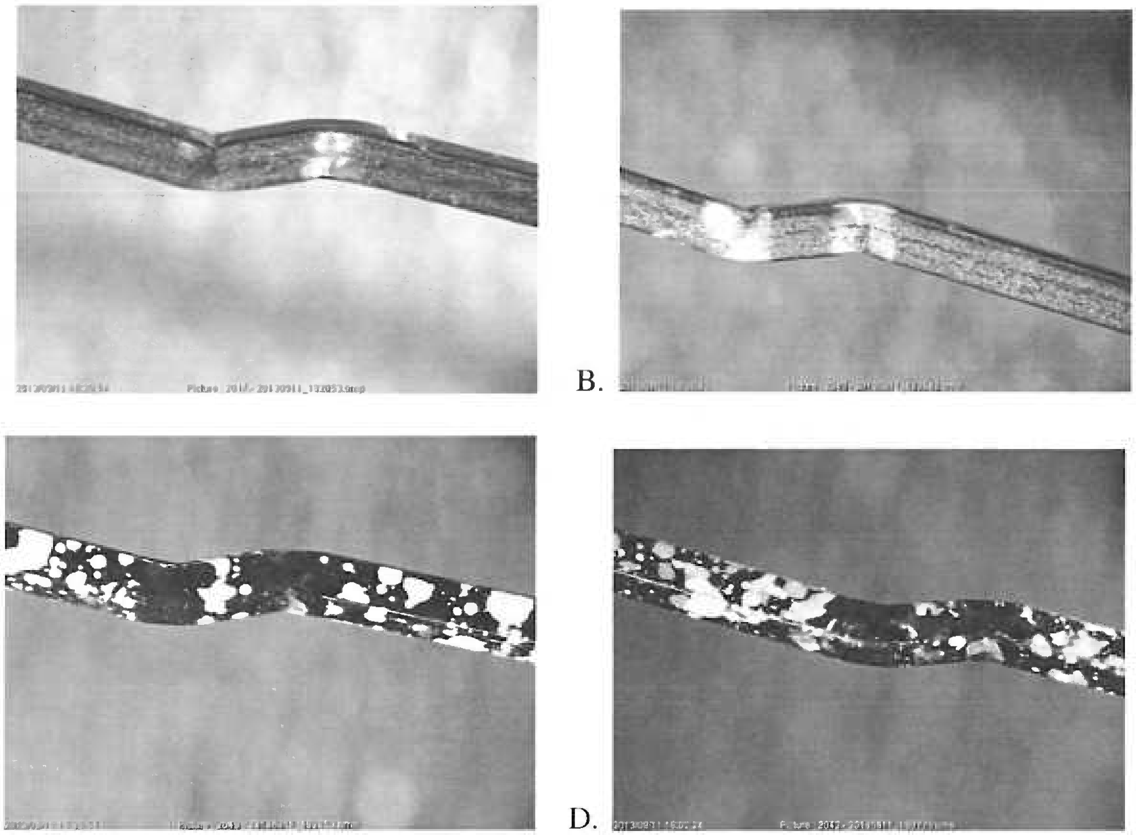
3/26/2013 HV mag WD HFW det
1:55:51 PM 10.00 kV 4 700 x 12.1 mm 31.7 µm ETD
10 µm




Resistance to Sliding
Work (grams mm)
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
AR
ALD
1 coat
2 coat

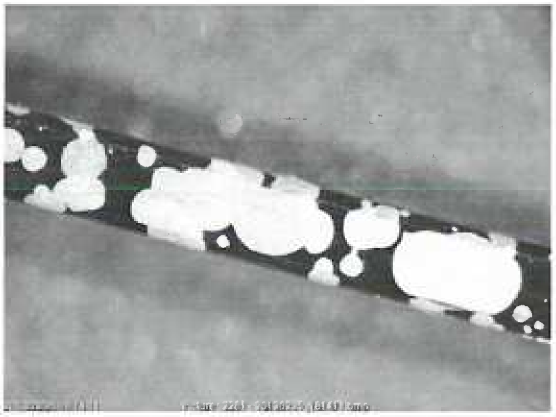

Mass Loss
Grams
0.0002
0.00015
0.0001
0.00005
0
-0.00005
AR
ALD
1 coat
2 coat

A) As-received stainless steel wire B) ALD coated stainless steel wire C) White pigmented ALD one-coat wire D) White pigmented ALD two-coat wire



A. B. C. D.

A) Facial surface of a white pigmented ALD one-coat wire after the bracket had been slid. B) Bracket side of the same wire after sliding.

A. 

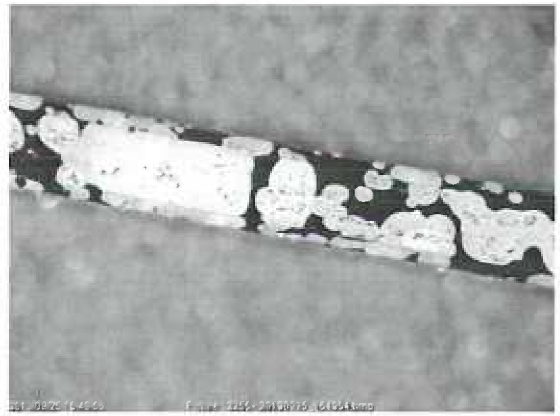
B. 

Table 1 – Ion Release Results

Ion Release (ppb)	*Al*	*Ti*	*Cr*	*Mn*	*Fe*	*Ni*	*Cu*
As-received							
Slid	6.93 (0.25)^{aBCD}	2.00 (0.16)^{aCD}	114.86 (49.95)^{aD}	11.01 (4.58)^{aCD}	583.91 (222.20)^{aCD}	45.09 (21.95)^{aCD}	10.49 (1.28)^{a}
Not slid	7.99 (0.78)^{bBCD}	1.84 (0.28)^{a}	90.29 (8.48)^{aCD}	9.39 (1.09)^{aCD}	495.29 (39.96)^{aCD}	34.24 (3.37)^{aCD}	10.58 (0.43)^{a}
ALD							
Slid	3902.29 (892.74)^{aACD}	1.05 (0.56)^{aCD}	130.24 (59.80)^{aD}	15.09 (5.76)^{aCD}	670.05 (281.90)^{aCD}	57.19 (25.17)^{aCD}	10.19 (1.60)^{a}
Not slid	3030.93 (968.05)^{bACD}	0.85 (0.51)^{aCD}	70.84 (48.10)^{aCD}	8.90 (4.36)^{aCD}	356.24 (243.88)^{aCD}	32.07 (20.01)^{aCD}	8.49 (0.75)^{a}
White Pigmented ALD one-coat							
Slid	15948.90 (3978.57)^{aAB}	4.24 (1.01)^{aABD}	305.27 (100.70)^{aD}	50.58 (7.65)^{aAB}	2988.26 (409.27)^{aABD}	294.52 (44.43)^{aABD}	20.76 (4.61)^{a}
Not slid	12620.38 (3346.44)^{bAB}	2.85 (0.20)^{bB}	604.36 (254.75)^{bAB}	70.55 (22.65)^{bAB}	4019.12 (1143.57)^{bAB}	427.76 (132.02)^{bAB}	18.66 (1.94)^{a}
White Pigmented ALD two-coat							
Slid	13695.65 (2865.10)^{aAB}	7.84 (1.91)^{aABC}	498.43 (48.14)^{aABC}	66.39 (3.98)^{aAB}	4241.26 (172.93)^{aABC}	429.53 (23.64)^{aABC}	24.10 (4.35)^{a}
Not slid	10619.63 (1493.70)^{bAB}	2.96 (0.72)^{bB}	475.86 (69.86)^{aAB}	63.31 (6.35)^{aAB}	4161.62 (236.30)^{aAB}	426.46 (25.76)^{aAB}	20.31 (2.07)^{a}

a and b, Different letters mean a statistically significant difference ($P<0.05$) between slid and not slid samples in each group (same column).

Upper case letters indicate significant differences ($P<0.05$) between the groups: A, vs as-received; B, vs ALD; C, vs white pigmented ALD-one coat; D, vs white pigmented ALD two-coat.

Literature Review

Resistance to Sliding

In orthodontic tooth movement using sliding mechanics, the orthodontist must overcome the mechanical force of friction, which opposes tooth motion. Friction is defined as the resistance to sliding. Kusy and Whitley further divide resistance to sliding into three components: friction, binding, and notching.[1]

Friction

Friction is the force resisting the motion between two surfaces.[2] In orthodontic tooth movement with conventional appliances, friction results from the interaction of the archwire with the sides of an orthodontic bracket or ligature.[3] In the passive configuration, the archwire does not contact the mesial and distal edges of the bracket slot and only friction contributes to the resistance to sliding. Classic friction is defined as the normal force applied by ligation multiplied by the coefficient of friction. Friction can be further divided into static and kinetic types of force.

Static friction is the force required to cause the initial movement of an object. Its magnitude must prevent motion between two surfaces, up to the point where it is overcome and movement takes place. Kinetic friction is the force that opposes the direction of motion and is always lesser in value than static friction. Kinetic friction is almost irrelevant in orthodontic tooth movement because continuous movement along an archwire rarely ever occurs.[3]

The coefficient of friction (COF), also known as "frictional coefficient," is symbolized by the Greek letter u. It is a dimensionless value and describes the ratio of the force of friction between two objects and the force pressing them together. The coefficient of friction depends upon the relative roughness of the contacting surfaces. As the asperities of one surface engage the other surface of the couple, roughness interlocking occurs. This results in surfaces that move less readily and an increase in friction. There is a coefficient of friction associated with both static and kinetic friction, and these will increase as the frictional force increases.[1]

Binding

When a force is applied to a bracket to move a tooth, the tooth tips in the direction of the force until the wire contacts the corners of the bracket. Binding is created when there is contact between the wire and the corners of the bracket and contributes to most of the resistance to sliding. Articolo and Kusy found the binding influence became greater as the wire-bracket angulation increased. [4] With a 7° angulation, binding made up 80% of the resistance to sliding whereas when the angle was increased to 13°, binding created 99% of the resistance to sliding and friction no longer had an influence.

Notching

Notching often occurs under clinical conditions when there is permanent deformation of the wire at the wire-bracket interface. When a notched wire engages the bracket corner, tooth movement stops until further elastic deformation of the wire occurs due to bone remodeling and bending during mastication, which displaces the teeth and eventually releases the notch.[3]

Effects on Orthodontic Treatment

The frictional force between the bracket and the archwire is an important consideration in clinical orthodontics because the orthodontic force must overcome the frictional resistance. Minimizing friction will help to reduce the levels of clinically applied force needed for moving teeth.[2] Lighter forces are more favorable to initiate and maintain tooth movement, result in less painful treatment and help maintain position of anchorage teeth. Excessive force can result in pain, lost anchorage, and unwanted tooth movements.[4] Furthermore by minimizing friction the treatment period may be reduced and help to obtain an optimal biological response for effective tooth movement.[2]

Mechanisms used to reduce friction

Friction during clinical tooth movement can be affected by the size and shape of the wire, bracket type, bracket and wire materials, angulation of the wire relative to the bracket, type of ligation, and whether the environment is wet or dry.[5]

Size and shape of the wire

Archwires are typically made in two configurations: round and rectangular. A wire with a smaller cross section will occupy less space in the bracket slot than a larger wire. Kusy and Whitley stated that a smaller wire will help to facilitate the initiation of sliding mechanics and lead to a decrease in frictional forces.[6,7] Several studies have shown that rectangular wires with larger slot contact areas generated greater frictional resistance than round wires in certain circumstances.[7,8] Drescher et al. reported that friction depended primarily on the vertical dimension of the wire and found an 0.016 inch Hi-T round wire and a 0.016 x 0.022 inch Hi-T rectangular wire had virtually the same amount of friction.[7]

Bracket width and style

The size of the bracket width can also affect friction. Frank and Nikolai found that frictional resistance increased with bracket width and recommended the use of edgewise wires with relatively high stiffness and narrow brackets to obtain the best results for canine retraction.[8] However, Drescher et al. evaluated stainless steel (Unitek), nitinol (Unitek), and beta titanium (Ormco) archwires with various wire dimensions and bracket widths of 2.2 mm, 3.3 mm, and 4.2 mm, and found that for each wire material, the narrow brackets (2.2 mm) generated the greatest frictional force.[7]

Conventional and self-ligating brackets are also both widely used in orthodontics. Thorstenson and Kusy evaluated a series of self-ligating brackets and conventionally ligated brackets to examine the effect of friction under dry and wet conditions. [9] For both conventional and self-ligating brackets, there was an increased resistance to sliding as the wire-bracket angulation increased. The resistance to sliding of the self-ligating brackets was found to be lower than those of the conventional brackets because of the absence of a ligation force.

The clinical advantage of a reduced resistance to sliding should be a reduction in the amount of treatment time, which has been investigated in many studies. Pandis et al examined the time needed to correct mandibular crowding with conventional edgewise brackets and Damon 2 self-ligating brackets, [10] and found no difference for the two types of brackets. Miles also performed a similar study and concluded the Damon 2 bracket was no more effective than a conventional bracket during initial alignment.[11]

Bracket Materials

Stainless steel is one of the most commonly used materials in orthodontic brackets due to its low cost and low reactivity. In the passive configuration, the frictional properties of stainless steel archwires and brackets make it the “gold standard” for orthodontic appliances. With the increasing demand for esthetics, various esthetic brackets have been developed and tested such as polycarbonate, polycrystalline alumina, and ceramic-reinforced polycarbonate.[12] Badakidou et al. compared the frictional forces between composite, ceramic, and metal brackets. The brackets with the highest friction were the two ceramic brackets made of polycrystalline ceramic and monocrystalline ceramic, respectively. Similarly, several other studies support the conclusion that ceramic brackets have a significantly higher frictional resistance than any other alloy combination.[13]

To overcome the poor frictional behavior of ceramic brackets, some manufacturers have inserted stainless steel slots into the ceramic bracket to improve their frictional and mechanical properties while retaining their esthetic appeal. Thortenson and Kusy evaluated polycarbonate, polycrystalline alumina, and ceramic-reinforced polycarbonate brackets with and without stainless steel inserts as well as stainless steel brackets to assess how the addition of the stainless steel slot affected friction. The frictional properties of esthetic brackets with the stainless steel inserts were between those of stainless steel brackets and conventional esthetic brackets without the stainless steel slot. However, the addition of the stainless steel slots did not considerably improve the resistance to sliding over the esthetic brackets without inserts. [12]

Ligation

Friction can also vary depending on the type of ligation used. Frank and Nikolai compared stainless steel and elastomeric ligation methods and found the frictional resistance increased as the ligature force applied to the wire increased. There was an insignificant difference between elastomeric ligation and a steel ligature tie force of 225 grams but the authors stated angulations and ligature forces should be kept small to minimize frictional resistance.[8]

Archwire Surface Texture

Several studies have evaluated the effect of surface roughness on friction. Kusy et al. demonstrated via laser spectroscopy that different archwire alloys have different surface roughness. Stainless steel appeared the smoothest, followed by cobalt-chrome (Elgiloy), beta-titanium (TMA) and nickel titanium.[14] Kusy further evaluated these wires and found no clear relationship between surface roughness and the coefficients of friction. While the surface roughness of stainless steel, cobalt-chrome, and nickel titanium archwires showed a slight positive correlation with frictional coefficients, the beta titanium archwires did not.[15] Doshi and

Bhad-Pati also found no correlation between wire roughness and frictional resistance. However they did find a positive correlation between bracket slot roughness and frictional resistance.[16]

Saliva

There is conflicting evidence in the literature as to whether saliva functions as a lubricant or as an adhesive when the archwire is slid through a bracket.[1] Both dry and wet states exist in the oral cavity and some in vitro studies have used human saliva or artificial saliva to assess its effect on friction. Kusy showed that when saliva is present, frictional forces and coefficients may increase, decrease, or not change depending on the archwire alloy tested. Polycrystalline alumina and stainless steel brackets were tested using stainless steel, cobalt-chromium, nickel titanium, and beta-titanium wires, and the greatest difference between dry and wet states occurred with beta-titanium archwires. The kinetic coefficient of friction in the wet state was reduced 50% compared to the value in the dry state. However, couples made of stainless steel wires and brackets suggested saliva may have an adhesive behavior in the wet versus the dry state.[17] In a similar study evaluating six alumina brackets and various archwire alloys, Saunders and Kusy found saliva tended to decrease the friction observed between titanium couples in each of the ceramic brackets tested.[18]

Esthetic Archwires

Having an esthetic archwire to complement esthetic brackets is becoming more desirable with the increasing trend of adult orthodontic patients and demand for esthetics. While much progress has been made in the development of esthetic brackets, the most effective wires continue to be fabricated from metal alloys.

Esthetic archwires have been explored using translucent polymeric wires.[19] Optiflex (Ormco Corp) was the first esthetic transparent nonmetallic orthodontic wire that contained a single-fiber structure made of a silica core and a silicone resin middle layer with a stain-resistant nylon outer layer.[20,21] While excellent in appearance, the mechanical properties of Optiflex were inferior to those of metal wires.[22] Furthermore, Jancar et al. reported the following possible modes of failure of fiber-polymer complex materials: transverse splitting, brittle tensile failure with fiber pullout, interfacial shear failure, and intralaminar shear failure.[23]

A fiber-reinforced plastic wire (FRP wire) using poly-methyl methacrylate for the matrix and biocompatible glass fibers for reinforcement has also been developed. The FRP wire was said to have optimal esthetics and similar mechanical properties to metal wires. The CPSA glass fibers were originally developed for use in orthopedic implant materials and have excellent biocompatibility, while the fibers are very flexible and elastic. Results showed stress-relaxation occurred rapidly in the first 15 minutes under both dry and wet conditions but slowly decreased thereafter.[21] Suwa et al. tested the FRP esthetic wire with various types of brackets and found the frictional characteristics of the FRP wire with brackets were similar to metal wires, except when used with the polycrystalline alumina bracket.[24]

Burstone et al. examined wires made out of polyphenylene, a polymer with an increased hardness and resistance to stress relaxation as well as good formability and translucency. The limitation of most polymers is stress relaxation or creep. Burstone et al. found that while the polyphenylene archwires had flexural properties similar to NiTi and beta-titanium wires, they did experience stress relaxation over time.[19] Goldberg et al. also tested polyphenylene wires and found the wires exhibited time-dependent behavior associated with viscoelastic properties, leading to stress relaxation and deformation with initial placement of the wire. Over time the force decreased and wire deformation increased. Goldberg et al. concluded that the wire required the orthodontist to understand and apply viscoelastic concepts to optimize its clinical use.[25]

Metal wires have also been coated with either tooth-colored polymers or inorganic materials to maintain mechanical properties and improve esthetics. Materials used in the coating process are often polytetrafluoroethylene (Teflon) or epoxy resin. However, many lack the translucency necessary for optimal esthetics and in some cases the outer coating can wear or peel and limit the bending of the wire. Neumann tested wires with Teflon coatings and found that regions peeled off during masticatory function testing, thus affecting the mechanical properties of the wire.[26] Elyyan et al. performed a randomized clinical trial of epoxy resin-coated nickel titanium wire and found the retrieved coated wires produced lower force values than as-received coated wires with 25% of the coating peeling off within 33 days in vivo, leaving large surface defects. Elyyan et al. stated the irregular surfaces could lead to plaque accumulation in surface defects and affect tooth movement should the defects lead to entrapment of the bracket edges.[27]

Recently new esthetic nickel-titanium wires with tooth color have been developed (Woowa). Woowa has a double-layered coating structure with an inner layer consisting of a silver and platinum coating and an outer layer made of a special polymer coating of parylene. The anterior region of Woowa is coated white and esthetic, with the posterior region is not-coated. Iijima et al. examined Woowa (polymer coating) and Bioforce High Aesthetic Archwire (metal coating) to determine the effect of the coatings on the mechanical properties of the esthetic wires. The surface of the parylene coating layer on Woowa had a rougher morphology and much lower hardness and modulus of elasticity than the noncoated portion. Iijima et al. concluded the coating layers might influence the frictional characteristics of Woowa.[20]

Atomic Layer Deposition

Coatings

In addition to esthetic coatings such as Teflon and epoxy resin, archwires have been coated to try to reduce the resistance to sliding and coefficient of friction. Diamond-like carbon coating (DLC)[5] and plasma-immersion ion implantation wires have been marketed for clinical orthodontics to improve friction but are not tooth-colored. Recent studies on DLC coatings of nickel-titanium and stainless steel wires showed less frictional resistance than as-received wires and a reduction of binding and notching due to the increased hardness of the DLC layer.[5] However DLC coatings can be prone to plastic deformation, cracks, and significant delamination.[28]

Ion-implantation of nickel has also been applied to the surface of orthodontic wires to decrease the static and kinetic coefficients of friction and better facilitate sliding.[29] Some studies have shown less frictional forces during tooth movement, while others have shown there were no significant differences between nickel-titanium wires with or without ion-implantion .[5] Kula et al. compared the rate of space closure using ion-implanted TMA archwires and non-implanted TMA archwires using a split mouth design. There was no significant difference in the rate of space closure between the two wires using non-implanted stainless steel brackets.[29] Ryan et al. compared the amount of tooth movement using different archwire compositions of stainless steel, nickel titanium (control and ion implanted) and beta titanium (control and ion implanted) with a standard edgewise bracket. Results showed the ion implantation process did reduce the frictional forces and the treated wires consistently and significantly produced greater tooth movement when compared with the corresponding untreated wire. The ion implantation process tended to increase stress fatigue, hardness, and wear regardless of the composition of the material.[30]

Atomic Layer Deposition

Atomic layer deposition is a chemical gas phase thin film deposition technique that deposits a highly uniform coating with excellent conformality and accurate film thickness control. Source vapors are pulsed into the reactor one at a time, separated by purging or evacuation periods. The wire is exposed to gaseous precursors repeatedly, as each exposure step saturates the surface with a monomolecular layer of that precursor in order to create a thin uniform coating that is covalently bound to the underlying metal.

In the ALD cycle, the film growth occurs in a cyclic manner. One cycle consists of four steps: (i) exposure of the first precursor, (ii) purge or evacuation of the reaction chamber, (iii) exposure of the second precursor and (iv) purge or evacuation. The cycle is repeated as many times as necessary to obtain the desired thickness of the coating.[31] To coat orthodontic wires, the first precursor, tri-methyl aluminum is added to the chamber where it reacts with the substrate oxide, releasing methane as a by-product. Excess tri-methyl aluminum and methane are removed from the chamber. Water vapor is then added to the chamber where it reacts to form Al-O bridges and hydroxyl groups, which will react with the next pulse of tri-methyl aluminum added to the chamber. One tri-methyl aluminum pulse and one water vapor pulse form one cycle.

ALD surface coatings offer many advantages, including: accurate and simple thickness control, large area and batch capability, excellent conformality, good reproducibility, and high quality materials obtained at low processing temperatures.[31] ALD also helps to increase the hardness of the material. Werner et al found the ALD-coated wire and bracket couple had the lowest resistance to sliding and a coefficient of friction significantly lower than as-received wires, and the ALD coatings did not delaminate during scratch testing.[32]

Corrosion

The use of coatings can also be applied to help combat corrosion of orthodontic appliances in the oral environment. Corrosion is an electrochemical process involving oxidation-reduction reactions that result in the loss of metal ions directly into solution and the deposition and possible dissolution of a surface film .[33] Most orthodontic appliances are made from a stainless steel alloy and contain 6-12% nickel and 15-22% chromium. Because these appliances are continuously exposed to saliva they are subject to corrosion. There is increasing concern about the corrosion of orthodontic appliances in the oral environment due to the possible localized or systemic effects from corrosion products.[34] Furthermore, corrosion can have an effect on the physical properties and clinical performance of orthodontic appliances because of its influence on friction.[33]

Stainless steel, cobalt-chromium, and titanium alloys used in orthodontic appliances rely on the formation of a passive surface oxide films to help prevent corrosion. However, the surface layer is susceptible to mechanical and chemical disruption, causing the oxide film to dissolve slowly. Acidic conditions and chloride ions can accelerate this process, thus a diet high in sodium chloride and acidic carbonated drinks can encourage the corrosion process.[34] The major corrosion products for stainless steel are iron, chromium, and nickel. Nickel is the most common cause of contact allergy and is known to trigger many allergic reactions. Furthermore, carcinogenic, mutagenic, and cytotoxic effects have also been attributed to nickel. Nickel is absorbed in the gastrointestinal tract and eliminated through the kidneys, with 90% excreted in urine.[33]

The level of corrosion of any metal and the release of ions depends on the solvent in which it is immersed, pH of the solution, and length of immersion. De Menezes and Quintao tested stainless steel, nickel-titanium (NiTi), and thermo NiTi archwires immersed in artificial saliva of different pH values during a 28-day period. The release of six different metal ions: titanium, chromium, nickel, iron, copper, and zinc, was determined using a high resolution mass spectrophotometer. The change in pH had a strong effect on the release of ions as did the wire composition and time of immersion. The largest number of ions was released during the first week with a gradual decline thereafter.[33]

To try to minimize corrosion, manufacturers have allowed alloy substitution or addition, coatings, or modifications to the production process. For stainless steel alloys, the addition of chromium and nickel enhances corrosion resistance. Chromium contributes to the surface oxide layer, which spontaneously forms in air and the oral environment to passivate the wire. Nickel competes with chromium to form salts, therefore making more chromium available. Coatings currently in use include titanium nitride to improve hardness and reduce friction or an epoxy resin to improve esthetics.[34]

The corrosion process of orthodontic appliances may be observed as a discoloration of enamel around the brackets due to the deposition of corrosion products. There may also be a progressive increase in corrosion product build up over time in the bracket slot, causing increased frictional resistance to sliding mechanics and adversely affect treatment progress. However, the corrosion process is often unnoticed and quantified only by the concentration of ions released into solution. The most frequently used solutions are saline (0.05% or 0.9%) or artificial saliva with different compositions.[33]

FUTURE RESEARCH

Results from this study demonstrate the potential for ALD coatings to be used in orthodontics. A more uniform method is needed to deposit the white pigment that would allow for better esthetics and reproducibility. Plasma coating is one possibility to ensure a uniform deposition of particles. Once the deposition technique is developed, further studies are needed to determine the optimal pigment and ALD thickness to achieve esthetics and maintain the mechanical properties of the stainless steel wire. It would also be interesting to see the effect of applying an esthetic coating only on the labial surface of the wire.

Future studies are also needed to compare the mechanical properties of pigmented ALD coated wires with other types of esthetic wires currently used in orthodontics. While there have been studies which have examined esthetic nickel-titanium coated wires there are fewer studies on esthetic stainless steel coated wires. The frictional resistance of pigmented ALD coated wires should also be compared to titanium-molybdenum alloy (TMA) wires to determine whether there is a clinical relevance for pigmented ALD coated wires.

More in vitro studies on corrosion of ALD coatings need to be done before a clinical study can be performed. This study should be replicated with a larger sample size to statistically confirm our findings. The experiment should also be repeated with alterations in the testing medium to look at the effects of pH, temperature, diet, fluoride, and other intraoral characteristics on the ion release of ALD coatings.

REFERENCES

1. Kusy RP, Whitley JQ. Friction Between Different Wire-Bracket Configurations and Materials. Sem in Ortho. 1997; 3:166-177.

2. Redlich M, Mayer Y, Lewinstein I. In vitro study of frictional forces during sliding mechanics of "reduced-friction" brackets. Am J Orthod Dentofacial Orthop. 2003; 124:69-73.

3. Burrow SJ. Friction and resistance to sliding in orthodontics: A critical review. Am J Orthod Dentofacial Orthop. 2009; 135: 442-447.

4. Articolo LC, Kusy RP. Influence of angulation on the resistance to sliding in fixed appliances. Am J Orthod Dentofacial Orthop. 1999; 115: 39-51.

5. Muguruma T, Iijima M, Brantley WA, Mizoguchi I. Effects of a diamond-like carbon coating on the frictional properties of orthodontic wires. Angle Orthod. 2011; 81: 141-48.

6. Kusy RP, Whitley JQ. Influence of archwire and bracket dimensions on sliding mechanics: derivations and determinations of the critical contact angles for binding. Eur J Orthod. 1999; 21: 199-207.

7. Drescher D, Bourauel C, Schumacher HA. Frictional forces between bracket and arch wire. Am J Orthod Dentofacial Orthop. 1989; 96: 397-404.

8. Frank CA, Nikolai RJ. A comparative study of frictional resistances between orthodontic bracket and arch wire. Am J Orthod. 1980; 78: 593-609.

9. Thortenson G, Kusy R. Resistance to sliding of self-ligating brackets versus conventional stainless steel twin brackets with second order angulation in the dry and wet (saliva) states. Am J Orthod Dentofacial Orthop. 2001; 120: 361-70.

10. Pandis N, Polychronopoulou A, Eliades T. Self-ligating vs conventional brackets in the treatment of mandibular crowding: a prospective clinical trial of treatment duration. Am J Orthod Dentofacial Orthop. 2007; 132: 208-15.

11. Miles PG, Weyant RJ, Rustveld L. A clinical trial of Damon2 vs conventional twin brackets during initial alignment. Angle Orthod. 2006; 76: 480-85.

12. Thorstenson G, Kusy R. Influence of Stainless Steel Inserts on the Resistance to Sliding of Esthetic Brackets with Second-Order Angulation in the Dry and Wet States. Angle Orthod. 2003; 73: 167-75.

13. Bazakidou E, Nanda RS, Duncanson MG, Sinha P. Evaluation of frictional resistance in esthetic brackets. Am J Orthod Dentofacial Orthop. 1997; 112: 138-44.

14. Kusy, RP, Whitley JQ, Mayhew MJ, Buckthal JE. Surface Roughness of Orthodontic Archwires via Laser Spectrscopy. Angle Orthod. 1988; 33-45.

15. Kusy RP, Whitley JQ. Effects of surface roughness on the coefficients of friction in model orthodontic systems. J Biomechanics. 1990; 23: 913-25.

16. Doshi UH, Bhad-Patil WA. Static frictional force and surface roughness of various bracket and wire combinations. Am J Orthod Dentofacial Orthop. 2011; 139: 74-79.

17. Kusy RP, Whitley JQ, Prewitt MJ. Comparison of the frictional coefficients for selected archwire-bracket slot combinations in the dry and wet states. Sem in Orthod. 1997; 3: 166-77.

18. Saunders CR, Kusy RP. Surface topography and frictional characteristics of ceramic brackets. Am J Orthod Dentofacial Orthop. 1994; 106: 76-87.

19. Burstone, CJ, Liebler SAH, Goldberg AJ. Polyphenylene polmers as esthetic orthodontic archwires. Am J Orthod Dentofacial Orthop. 2011; 139: e391-98.

20. Iijima M, Muguruma T, Brantley WA, Choe HC, Nakagaki S, Alapati SB, Mizoguchi I. Effect of coating on properties of esthetic orthodontic nickel-titanium wires. Angle Orthod. 2012; 82: 319-25.

21. Imai T, Watari F, Yamagata S, Kobayashi M, Nagayama K, Nakamura S. Effects of water immersion on mechanical properties of new esthetic orthodontic wire. Am J Orthod Dentofacial Orthop. 1999; 116: 533-38.

22. Talass MF. Optiflex archwire treatment of a skeletal Class III open bite. J Clin Orthod 1992; 26: 245-52.

23. Jancar J, Dibenedetto AT, Goldberg AJ. Thermoplastic fiber-reinforced composites for dentistry. Part II. Effect of moisture on flexural properties of unidirectional composites. J Mater Sci 1993; 4: 562-8.

24. Suwa N, Watari F, Yamagata S, Iida J, Kobayashi M. Static-Dynamic Friction Transition of FRP Esthetic Orthodontic Wires on Various Brackets by Suspension-Type Friction Test. J of Biomedical Research. 2002; 67B: 765-771.

25. Goldberg AJ, Liebler SAH, Burstone CJ. Viscoelastic properties of an aesthetic translucent orthodontic wire. Eur J Orthod. 2011; 33: 673-78.

26. Neumann P, Borauel C, Jager A. Corrosion and permanent fracture resistance of coated and conventional orthodontic wires. Journal of Materials Science. 2002; 13: 141-47.

27. Elyyan F, Silikas N, Bearn D. Ex vivo surface and mechanical properties of coated orthodontic archwires. Eur J Orthod. 2008; 30:661-67.

28. Zhang TH, Huan Y. Nanoindentation and nanoscratch behaviors of DLC coatings on different steel substrates. Composites Science and Technology. 2005; 65: 1409-13.

29. Kula K, Phillips C, Gibilaro A, Proffit WR. Effect of ion implantation of TMA archwires on the rate of orthodontic sliding space closure. Am J Orthod Dentofacial Orthop 1998. 114: 577-79.

30. Ryan R, Walker G, Freeman K, Cisneros GJ. The effects of ion implantation on rate of tooth movement: An in vitro model. Am J Orthod Dentofacial Orthop 1997. 112: 64-68.

31. Ritala M, Leskela M. Handbook of Thin Film Materials. Chapter 2: Atomic Layer Deposition. 2001, 103-55.

32. Werner G, Smith S, Conley J, Mitchell JC. Atomic Layer Deposition Coated Orthodontic Archwires to Reduce Coefficient of Friction. MS Thesis.

33. De Menezes LM, Quintao CCA. The Release of Ions from Metallic Orthodontic Appliances. Sem in Orthod. 2010; 4: 282-92.

34. House K, Sernetz F, Dymock D, Sandy JR, Ireland, AJ. Corrosion of orthodontic appliances—should we care? Am J Orthod Dentofacial Orthop 2008.133: 584-92.