Composition, Phase Structure, and Corrosion of Nickel-Free and Nickel-Containing Stainless Steel Orthodontic Wires

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COMPOSITION, PHASE STRUCTURE, AND CORROSION OF NICKEL-FREE AND NICKEL-CONTAINING STAINLESS STEEL ORTHODONTIC WIRES

by

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ABSTRACT
COMPOSITION, PHASE STRUCTURE, AND CORROSION OF NICKEL-FREE AND NICKEL-CONTAINING STAINLESS STEEL ORTHODONTIC WIRES

Amrita Rakalla, DDS

Marquette University, 2014

Stainless steel wires have long been used in orthodontics. The austenitic stainless steel used in orthodontics contains approximately 18 wt% chromium and 8 wt% nickel. Nickel improves the corrosion resistance and helps maintain the austenite structure of stainless steel. Nickel is the most allergenic metal and is the most common metal associated with contact dermatitis in orthodontics. Nickel-free wires have been developed, and it was the goal of this study to compare nickel-free and nickel-containing stainless steel orthodontic wires to determine and compare their composition, phase structure, and corrosion properties.

For each test, nickel-free and conventional stainless steel wires were compared from four companies: Acme Monaco, Dentaurum, Leone, and Scheu-Dental. Phase structure was determined using x-ray diffraction. Composition was measured using scanning electron microscopy with energy dispersive spectroscopy. For each wire, straight lengths were sectioned into 1-inch segments, arranged side-by-side, to create a 1-inch by 1-inch planar array of wires secured with sticky wax. Resultant XRD pattern peaks were indexed using standard methods or via ICDD files. Electrochemical corrosion tests were completed using a 3-electrode cell with a potentiostat and Gamry corrosion test software. Fusayama-Meyer artificial saliva solution was used as the electrolyte at room temperature. For each wire brand, wire lengths were isolated using nail polish, exposing a consistent surface area to account for varying diameters of the wires among brands. Open circuit potential, polarization resistance, and corrosion current density were determined. Data were compared using one-way analysis of variance (ANOVA) at a 0.05 significance value with a Tukey's Studentized Range (HSD) Test post hoc analysis, where required.

Two nickel-free wires had detectable amounts of nickel. All nickel-free stainless steel wires had an increased amount of manganese, chromium, and molybdenum with decreased iron content. The orthodontic stainless steel wires are mostly austenitic, but martensite may be present in both types. Although there were significant differences among the wires for the three corrosion parameters, there was not a general difference between nickel-free and conventional stainless steel wires. Overall, despite composition

differences between the nickel-free and nickel-containing stainless steel wires, they generally had the same phase structure and similar corrosion properties.

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CHAPTER 1
INTRODUCTION

Wires have multiple uses in orthodontics. Archwires are used in conjunction with brackets to move and align teeth, larger wires are used to fabricate orthodontic appliances, and others are used as retainers to prevent orthodontic relapse. There are several compositional types of orthodontic wires, including stainless steel, nickel-titanium, beta-titanium, and cobalt-chromium; each used for a different purpose due to certain desirable properties. Stainless steel wires have long been used in orthodontics for several reasons: high resistance to corrosion, high strength and springiness, ability to be easily formed and manipulated (through cold working and annealing during the manufacturing process), and low cost (Nie et al., 2011; Proffit, 2013).

The composition of stainless steel can vary greatly with over 100 variations developed (Verstrynge et al., 2006), but the austenitic stainless steel used to make most orthodontic products contains approximately 18 wt% chromium and 8 wt% nickel (Barrett et al., 1993). This is classified as AISI (American Iron and Stainless Steel Institute) type 304 (Daems et al., 2009). Stainless steel's high resistance to corrosion is mostly due to the significant amount of chromium present. Chromium oxide forms a passive layer over the surface of the steel, preventing oxygen from penetrating the alloy (Ortiz et al., 2011). Increased corrosion reduces biocompatibility and may hinder orthodontic treatment progress as a result of increased friction between the archwire and bracket (Widu et al., 1999). Molybdenum is added to stabilize the chromium, and copper is present in low amounts, adding to the corrosion resistance. Nickel forms salts that prevent chromium salts from forming, which leaves more chromium to form the passive layer. Nickel also provides firmness and ductility to stainless steel (Ortiz et al., 2011) and acts as an austenite stabilizer, making the austenitic form more stable at lower temperatures (Kusy, 1997; Eliades and Athanasiou, 2002). Carbon, manganese, silicon, phosphorus, and sulfur are also present in small amounts.

Of known metals, nickel is the most allergenic. Nickel sensitivity has an incidence between 10 to 20% of the population (Wataha, 2003), and nickel is also the most common metal associated with contact dermatitis in orthodontics (Rahilly and Price, 2003). Patients previously sensitized to nickel, most frequently due to body piercings, may be more likely to have an allergic response to nickel-containing orthodontic materials (Rahilly and Price, 2003), such as metal orthodontic brackets and wires. Alternatives to nickel-containing materials in orthodontics include ceramic or resin-based brackets and wires, beta-titanium wires, and nickel-free stainless steel brackets and wires. Common oral manifestations of a nickel allergy include a burning sensation, glossitis, gingivitis, gingival hyperplasia, erythema multiforme, metallic taste, and lip peeling (Staerkjaer and Menné, 1990; Bishara et al., 1993; Lindsten and Kurol, 1997; Janson et al., 1998).

Composition

Nickel-free orthodontic wires usually do not contain zero percent nickel, but rather a significantly reduced amount of nickel. For example, BioDur 108 Alloy is a low-nickel stainless steel with 0.10% nickel (Verstrynge et al., 2006). In order to maintain similar desirable properties to traditional stainless steel, the composition of nickel-free stainless steel must be altered. It is important to identify the exact composition of these wires as composition influences phase structure and multiple properties, including corrosion.

Phase structure

As stated above, the stainless steel used in orthodontic wires is usually austenitic stainless steel with 8% nickel. Altering the composition by reducing the nickel content may affect the phase structure. In the case of the BioDur 108 alloy, for example, the level of nitrogen is increased to maintain the austenitic phase structure (Zardiackas et al., 2003).

Corrosion

According to ISO standards, corrosion is identified as a “physicochemical interaction between a metal or an alloy and its environment that results in a partial or total destruction of the material or in a change of its properties” (ISO, 2001). Nickel adds to the corrosion resistance of stainless steel; therefore, nickel-free stainless steel wires may demonstrate increased corrosion. It is important to address this potential property change, as reduced corrosion rate is a desired property in orthodontic archwires. Corrosion of orthodontic materials, including stainless steel, has been studied extensively with various reports demonstrating potential cytotoxic effects (Eliades et al., 2004; Eliades, 2007). Several studies have demonstrated that even nickel-free wires may release nickel due to the presence of nickel in trace amounts (Rose et al., 1998; Schuster et al., 2004; Arndt et al., 2005; Milheiro et al., 2012) as well as demonstrate cytotoxic effects such as DNA damage (Fernández-Miñano et al., 2011) and inhibiting cell proliferation (Rose et al., 1998).

It was the goal of this study to compare nickel-free stainless steel and nickel-containing stainless steel orthodontic wires to determine and compare their composition, phase structure, and corrosion potential.

CHAPTER 2
LITERATURE REVIEW

Tooth movement occurs when prolonged pressure is applied to a tooth and the surrounding bone remodels (Proffit, 2013). In modern orthodontics, there are several ways this can be achieved. Most commonly, an orthodontic archwire is engaged in brackets bonded to the teeth. As the deflected wire is engaged, the force is transmitted to the bracket and indirectly to the tooth itself (Nikolai, 1997). Clear aligners are also used to produce tooth movement, but their effect is limited and less reliable. Tooth movement is best achieved with a light, continuous force (Proffit, 2013).

History of Orthodontic Archwires

Orthodontic archwires have evolved significantly since the initiation of orthodontics in the late 1800s. Edward Angle, the father of modern orthodontics, developed the E-arch in 1887. This appliance consisted of a rigid labial wire extending around the arch, attached only to the molar bands. The wire, made of either nickel-silver or platinum-gold, had a dimension of 0.032 or 0.036 inches. Nuts were placed on the threaded ends of the archwire to allow the wire to be expanded, and teeth were ligated to the wire individually (Nikolai, 1997; Proffit, 2013). However, this appliance was limited as it only allowed the teeth to be tipped into position. Angle then began putting bands on all of the teeth. Each band had a rectangular vertical slot behind a vertical tube (Proffit, 2013). The round archwire was rolled to form a ribbon arch, which was a gold wire with dimensions of 0.020 x 0.050 inches (Nikolai, 1997). The wire was held in the vertical slot with pins. Although this wire was more effective at controlling tooth movement, it still lacked the ability of torque control and root positioning. Angle made a breakthrough in 1928 with the development of the edgewise appliance. Instead of a vertical slot, Angle reoriented the slot 90 degrees. The slot had dimensions of 0.022 x 0.028 inches, and either round or rectangular archwires made of precious metal alloys were used. This appliance led to the development of currently used archwires and allowed control of individual tooth movement in all three planes of space as desired (Proffit, 2013).

Stainless Steel Wires

Modern wires have developed for different purposes in orthodontic treatment. No single wire is ideal for all phases of treatment, but wires should have certain desirable properties. These properties include high strength, low stiffness, high range, high formability, weldability, resilience, springback, and biocompatibility (Kusy, 1997; Proffit, 2013). Stainless steel wires were introduced to orthodontics in the late 1920s and soon replaced precious metal alloys due to increased strength and springiness, greater elastic modulus, ductility, better resistance to corrosion, and lower cost (Nikolai, 1997). Orthodontic stainless steel wires are typically AISI type 302 or 304 with a composition of 17-20% chromium, 8-12% nickel, 0.08-0.15% carbon, and iron forming the balance. These types are also referred to as 18-8 stainless steel, based on the chromium and nickel content. There may also be small amounts of manganese, silicon, phosphorus, sulfur, nitrogen, molybdenum, copper, and cobalt (Brantley, 2003).

There are three main types of stainless steel: ferrite, martensite, and austenite. The classification depends on the crystal structure of iron atoms. Ferrite is characterized by a body-centered cubic crystal, martensite is organized in a body-centered tetragonal crystal, and austenite is a face-centered cubic crystal. It should be noted, however, that the martensite phase in orthodontic stainless steel wires has been characterized as body-centered cubic (Khier et al., 1988). Orthodontic stainless steel is typically the austenitic form, which is the most corrosion resistant. The austenitic stainless steel is formed with the addition of nickel. Austenitic stainless steel has other desirable properties compared to the ferritic and martensitic forms. Austenitic stainless steel has greater ductility. It can undergo a greater degree of cold working, which strengthens it considerably. It is more easily formed and has greater weldability (Brantley, 2003).

The addition of 12-30 wt% chromium to iron forms the stainless steel alloy. When exposed to an oxidizing environment, chromium oxide forms a passive layer on the surface, preventing oxygen from penetrating the alloy and providing resistance to tarnish and corrosion (Brantley, 2003; Ortiz et al., 2011). Preventing corrosion is important to maintain biocompatibility and reduce the amount of friction between the archwire and bracket that may hinder orthodontic tooth movement (Widu et al., 1999). Molybdenum and nickel add to the corrosion resistance of stainless steel. Molybdenum acts to stabilize the chromium, while nickel forms salts that use up ions to prevent chromium salts from forming, thereby allowing more chromium to form the passive layer (Ortiz et al., 2011). Nickel also adds to the alloy’s firmness and ductility (Ortiz et al., 2011) and stabilizes the austenite phase structure at lower temperatures (Kusy, 1997; Eliades & Athanasiou, 2002).

Australian wire is a different type of stainless steel that has high resiliency and toughness, historically used in the Begg technique. Australian wire differs in composition from traditional stainless steel wires with 10 times more carbon (Pelsue et al., 2008). The increased carbon content contributes to hardness but also makes Australian wire more brittle.

Nickel Allergy, Corrosion, and Nickel-Free Stainless Steel

Of all metals, nickel is the most allergenic to humans with an incidence between 10 to 20% (Wataha, 2003). Nickel is also the most common metal associated with contact dermatitis in orthodontics (Rahilly and Price, 2003). The percentage of orthodontic patients who exhibit an allergic reaction to nickel is unknown, but one study determined that 17.2% of their sample (16 out of 93 patients) were allergic to nickel, based on patch testing (Pazzini et al., 2009). Patients allergic to nickel may not always elicit an oral mucosal response (Staerkjaer and Menné, 1990), but several case reports have documented that this can occur (Temesvári and Rácz, 1988; Trombelli et al., 1992; Veien et al., 1994; Kerosuo and Kanerva, 1997). Females are more likely to exhibit hypersensitivity, perhaps due to more exposure from nickel-containing jewelry; however, the incidence of nickel allergy in males is increasing (Wataha, 2003). Other sources of nickel exposure that may contribute to sensitization are cosmetics, detergents, the professional environment, and dentistry (Janson et al., 1998; Schuster et al., 2004). Patients who have been previously sensitized to nickel may be more likely to have an allergic reaction to nickel-containing orthodontic materials (Rahilly and Price, 2003). The allergic response is a type IV allergic reaction, or delayed-type hypersensitivity. This type of reaction is mediated by T cells, primarily CD4+ T cells. Langerhans cells present the antigen to CD4+ T cells, which then activate memory CD4+ cells in the lymph nodes. Memory cells were created from previous exposure and sensitization to nickel. These CD4+ T cells secrete various cytokines that increase the permeability of blood vessels, causing edema and allowing neutrophils, monocytes, and macrophages to infiltrate the nearby tissues. Enzymes from these cells can damage the tissue and cause necrosis (Bakula et al., 2011). The oral mucosa may have a diminished allergic response compared to the skin for several reasons: Saliva may remove the allergen before it reaches a certain threshold; the oral mucosa is highly vascular and may disperse the allergen; and the lack of a stratum corneum in the oral mucosa provides fewer antigen-presenting cells to elicit an immune response (Setcos et al., 2005). A nickel allergy can exhibit both intraoral and extraoral manifestations including a burning sensation, glossitis, gingivitis, gingival hyperplasia, erythema multiforme, metallic taste, and lip peeling (Staerkjaer and Menné, 1990; Bishara et al., 1993; Lindsten and Kurol, 1997; Janson et al., 1998). Because some intraoral manifestations resemble periodontal inflammation, nickel allergy may not be identified initially since poor oral hygiene around orthodontic appliances can cause a similar appearance of the periodontal tissues.

According to ISO standards, corrosion is identified as a "physicochemical interaction between a metal or an alloy and its environment that results in a partial or total destruction of the material or in a change of its properties" (ISO, 2001). An allergic response to nickel can occur when nickel ions are released from the alloy through corrosion, making them available to interact with the surrounding tissues (Wataha, 2000). Corrosion of stainless steel in orthodontics has been studied extensively, and various reports have demonstrated its potential cytotoxic effects (Eliades et al., 2004; Eliades, 2007; Ortiz et al., 2011). Due to biocompatibility concerns, nickel-free stainless steels have been introduced more recently. Typically, these alloys still have some nickel, but a significantly decreased amount. Because nickel is an important component of conventional austenitic stainless steel, the absence or minimal amount of nickel may affect certain properties, such as phase structure and resistance to corrosion.

Corrosion of conventional stainless steel has been studied extensively in orthodontics with various studies demonstrating potential cytotoxic effects (Eliades et al., 2004; Eliades, 2007). Nickel-free stainless steel has been studied considerably less, but several studies have demonstrated that these wires still release nickel because it is still present in trace amounts (Rose et al., 1998; Schuster et al., 2004; Arndt et al., 2005; Milheiro et al., 2012). Nickel-free stainless steel brackets may demonstrate cytotoxic effects such as DNA damage (Fernández-Miñano, et al., 2011; Ortiz et al., 2011), and the release from wires may inhibit cell proliferation (Rose et al., 1998).

CHAPTER 3
MATERIALS AND METHODS

For each test, nickel-free stainless steel and conventional stainless steel wires were compared. Wires of each type were obtained from four companies. From Acme Monaco (New Britain, CT, USA), their Ultra Low Nickel stainless steel (Acme Ni-Free) and bright stainless steel archwires (Acme SS), size 0.018” (0.45 mm), were compared. Dentaurum (Ispringen, Germany) has a low nickel stainless steel wire called Noninium that was compared to their Remanium stainless steel wire with diameters of 0.016” (0.40 mm). Leone (Florence, Italy) has a low nickel stainless steel product called Biosteel that was compared with Leowire, a stainless steel wire in size 0.024” (0.60 mm). Menzanium from Scheu-Dental (Iserlohn, Germany) is a nickel-free stainless steel wire that was compared to their stainless steel wire (Chromium) with a diameter of 0.024” (0.60 mm). It was not possible to obtain wires of the same diameter from all companies because a common size was not offered. All wires were straight lengths except the wires from Acme Monaco in the form of archwires and from Leone in the form of spools. Wires were tested as-received from the manufacturers.

Phase structure was determined by using x-ray diffraction (XRD). For each wire brand, multiple straight lengths of wire were sectioned into 1-inch segments, arranged side-by-side, to create a 1-inch by 1-inch planar array of wires secured with sticky wax (n = 2/wire brand) (Figure 1). The specimens were analyzed with an x-ray diffractometer (D8 Advance, Bruker Corp., Billerica, MA, USA) using Cu-Kα radiation at a voltage of 40 V, a current of 30 mA, with a scanning rate of 0.02°/s over a scan range (2θ angle) of 35 to 100° in a 72 minute period. The wires were analyzed at the surface, with the beam parallel to their long axes. Resultant XRD pattern peaks were indexed using standard methods or via ICDD files (International Center for Diffraction Data, Swarthmore, PA, USA). X-ray diffraction determines the crystal structure (austenite, martensite, ferrite, etc.) of the wires and was used to determine if the omission of nickel from the composition changed the crystal structure of the wires compared to standard stainless steel (Khier et al., 1988).

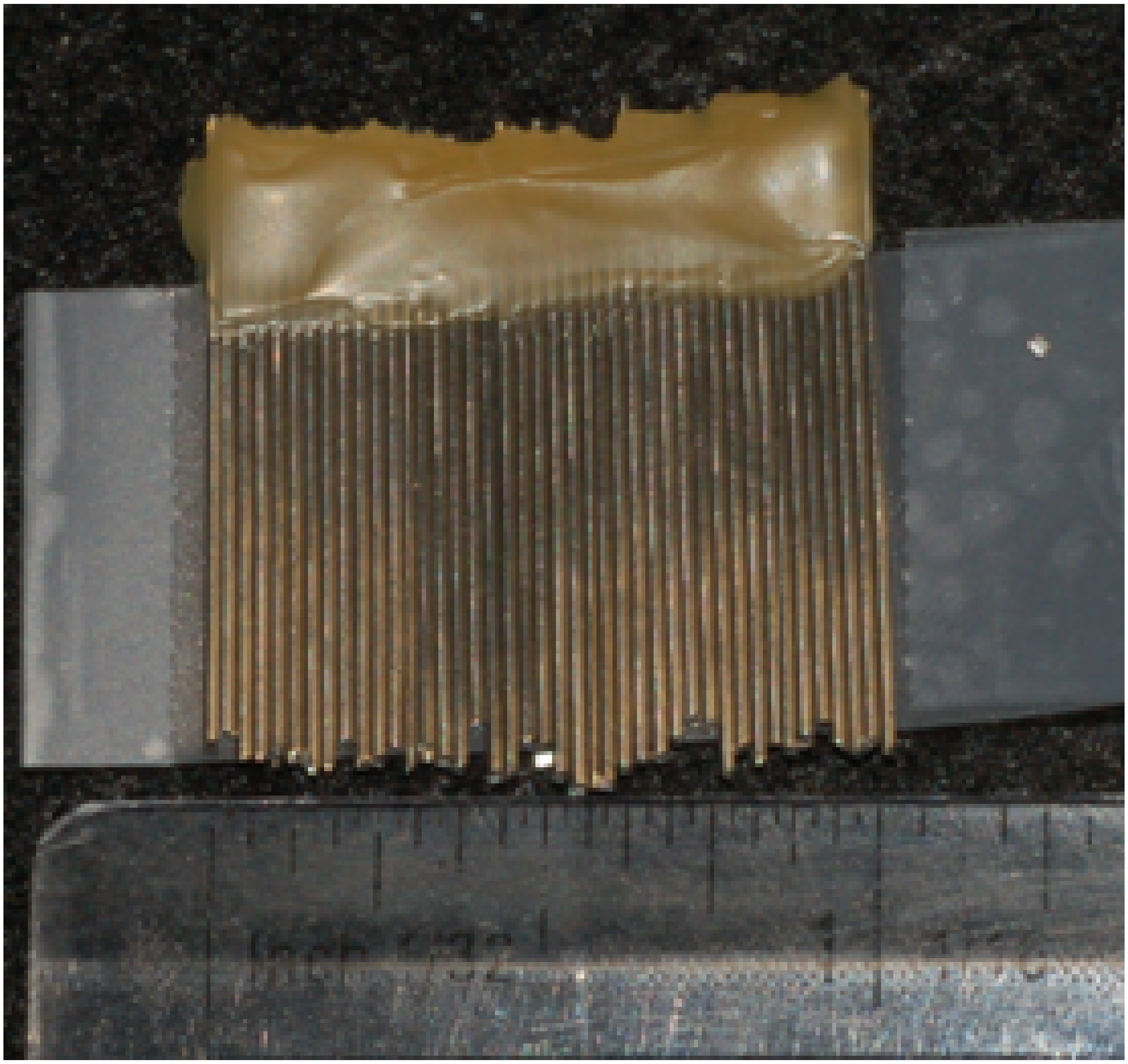

Figure 1. Wire configuration for XRD and EDS analysis

Composition was measured using scanning electron microscopy (SEM; JSM 6610LV, Jeol Ltd, Tokyo, Japan) with energy dispersive spectroscopy (EDS; Oxford Instruments, Abingdon, UK). Wire samples were prepared in the same planar array (n = 2/wire brand) used for the XRD analysis. One wire from each mounting was removed and cleaned in an ultrasonic bath for 10 minutes prior to SEM analysis. SEM imaging was performed at the surface of each wire using backscattered electrons (BE) at a voltage of 25 kV, a current of 78 µA, and at 1000X and 3000X nominal magnifications. For the EDS analysis, the wires were analyzed at the surface in the collecting window (120 x 90 µm) at a voltage of 25 kV, an acquisition time of 200 seconds, and a working distance of 11 mm. To identify the elemental composition in different areas where BE SEM analysis revealed a contrast in mean atomic number, spot analysis was carried out under the same conditions. Results are expressed in wt% for major (Fe, Cr, etc.) and minor elements. Composition determination shows which element(s) replaced nickel in the composition of the nickel-free wires.

Electrochemical corrosion tests were completed using a 3-electrode cell with a potentiostat and Gamry corrosion test software (PC4, Gamry Instruments, Warminster, PA, USA). A saturated calomel electrode (SCE; Gamry Instruments) served as the reference electrode and graphite was used as the counter electrode. Fusayama-Meyer artificial saliva solution (pH = 5.8) was used as the electrolyte at room temperature and was made with the following composition: KCl (0.4 g/L), NaCl (0.4 g/L), $CaCl_2$ (0.6 g/L), NaH_2PO_4 (0.690 g/L), $Na_2S\cdot 9H_2O$ (0.005 g/L), and urea (1 g/L). For each wire brand (n = 8/wire), wire lengths were isolated using nail polish, exposing a consistent surface area (0.71 cm^2) to account for varying diameters of the wires among brands (Figure 2).

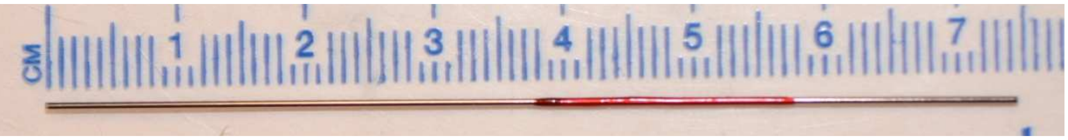

Figure 2. Wire isolated with nail polish

Electrochemical corrosion testing was comprised of three steps (Segal et al., 2009; Knutson and Berzins, 2013). Initially, the open circuit potential (OCP) was monitored for two hours. Second, a linear polarization test was performed. In this component, the current was measured while the potential of the wire was scanned at 0.05 mV/s from -20 to +25 mV (versus OCP). This test determines the polarization resistance (R_p), a measure of how easily the metal alloy electrochemically oxidizes during the application of an external potential. The final component is a cyclic polarization scan conducted between -300 to +700 mV (versus OCP) at a scan rate of 1 mV/s. This test determines the corrosion current density (or I_{corr}), which indicates how much the alloy corrodes.

Data were compared using one-way analysis of variance (ANOVA) at a 0.05 significance value with a Tukey's Studentized Range (HSD) Test post hoc analysis, where required. SAS software (SAS Institute, Cary, NC, USA) was used to perform the statistical analysis.

CHAPTER 4
RESULTS

Table 1 shows the composition results of the EDS analysis by element (wt%) for all wires tested. This can be compared to the information in Table 2, which is the elemental composition of each wire provided by the manufacturer.

Table 1. EDS analysis of elemental composition (wt%)

Material	Fe	Cr	Ni	Mo	Mn	Si	Al	Cu	V
Acme Ni-Free	53.2	22.0		0.8	23.4	0.3	0.3		
Acme SS	70.7	18.8	7.9	0.4	1.3	0.3	0.3	0.3	
Noninium	53.1	22.0		0.9	23.4	0.3	0.2	0.1	
Remanium	70.9	17.9	8.2	0.4	1.1	1.0	0.3	0.2	
Biosteel	61.9	20.0	0.2	2.8	13.8	1.0	0.2	0.1	
Leowire	71.2	17.5	8.4	0.7	1.2	0.4	0.3	0.2	0.1
Menzanium	65.4	19.5	0.2	2.5	13.7	0.7	0.3		
Chromium	70.3	18.1	7.9	0.6	1.4	1.0	0.3	0.4	

Biosteel and Menzanium still have detectable amounts of nickel. The nickel-free wires have a significantly higher percentage of manganese and a lower percentage of iron compared to the conventional stainless steel wires. They also tend to have slightly more chromium and molybdenum.

Table 2. Elemental composition as provided by manufacturers

Material	**Fe**	**Cr**	**Ni**	**C**	**Mo**	**Mn**	**Si**	**P**	**S**	**Other**
Acme Ni-Free	Bal	21.0	≤0.1	≤0.08	0.7	23.0	≤0.75	≤0.03	≤0.01	Cu ≤0.25, N 0.97
Acme SS	Bal	18.0-20.0	8.0-10.5	0.08		2.0	1.0	0.045	0.03	
Noninium	Bal	16.0-20.0	≤0.2	≤0.1	1.8-2.5	16.0-20.0	≤1.0	≤0.05	≤0.05	V≤0.2, N 0.7-1.0
Remanium	Bal	18.0-20.0	8.0-10.5	≤0.08		≤2.0	≤1.0	≤0.045	≤0.03	
Biosteel	Bal	18.0	0.2		2.0	18.0				N 1.0
Leowire	N/A									
Menzanium	Bal	16.0-20.0	≤0.2	≤0.1	1.8-2.5	16.0-20.0	≤1.0	≤0.005	≤0.05	V≤0.2, N 0.7-1.0
Chromium	Bal	18.0-20.0	6.0-9.0	≤0.12	≤0.8	≤2.0	≤1.5	≤0.045	≤0.03	

Figures 3 to 6 show the indexed XRD patterns of all wires tested. Austenite (γ phase) and martensite (α′ phase) were the main phases identified in the analysis.

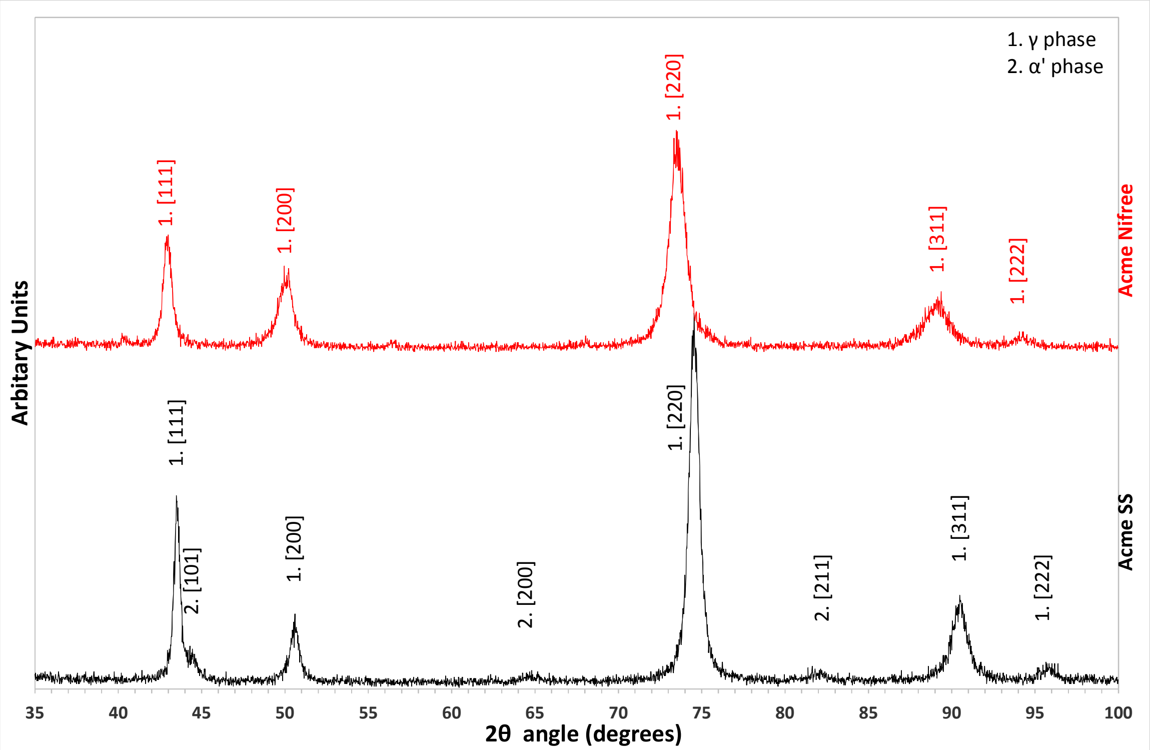

Figure 3. Indexed XRD patterns of Acme Monaco Ni-Free and Acme SS wires

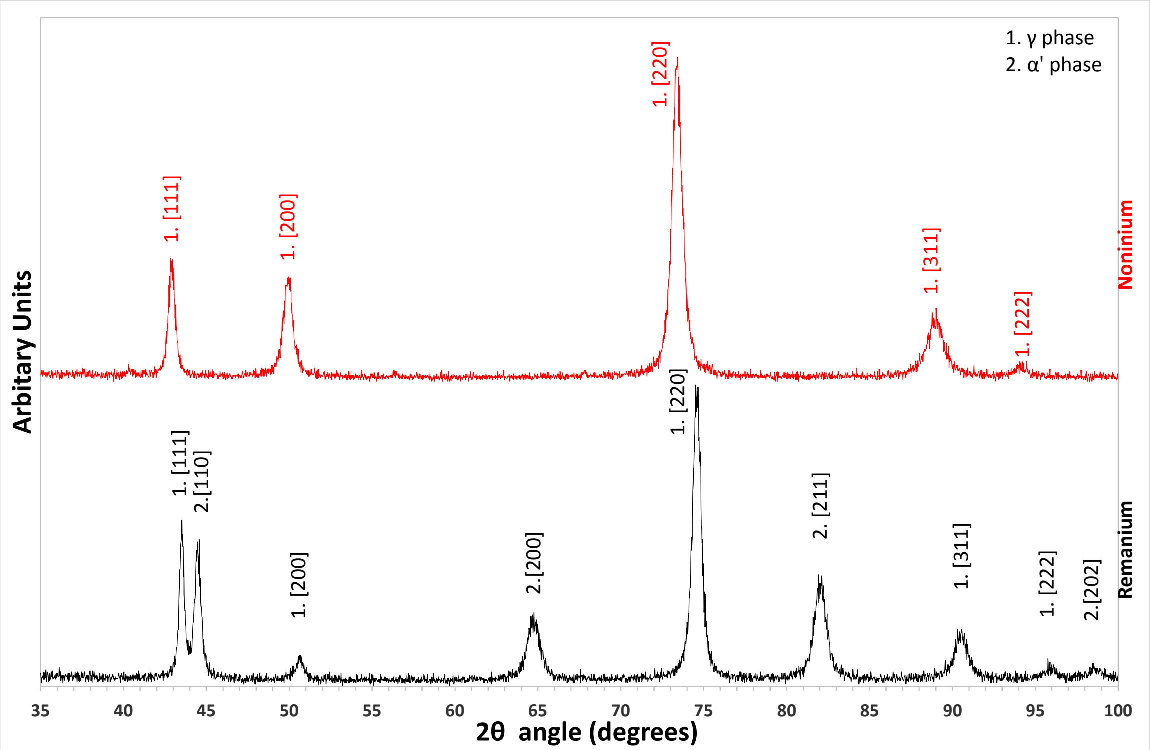

Figure 4. Indexed XRD patterns of Dentaurum Noninium and Remanium wires

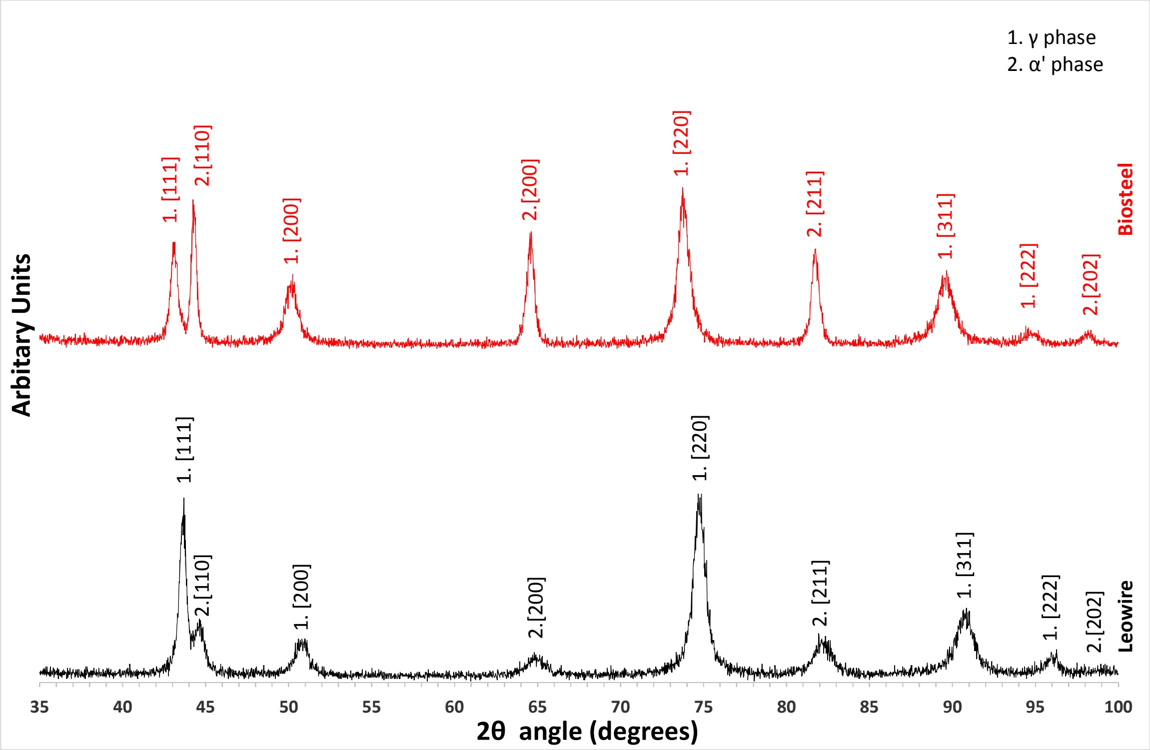

Figure 5. Indexed XRD patterns of Leone Biosteel and Leowire wires

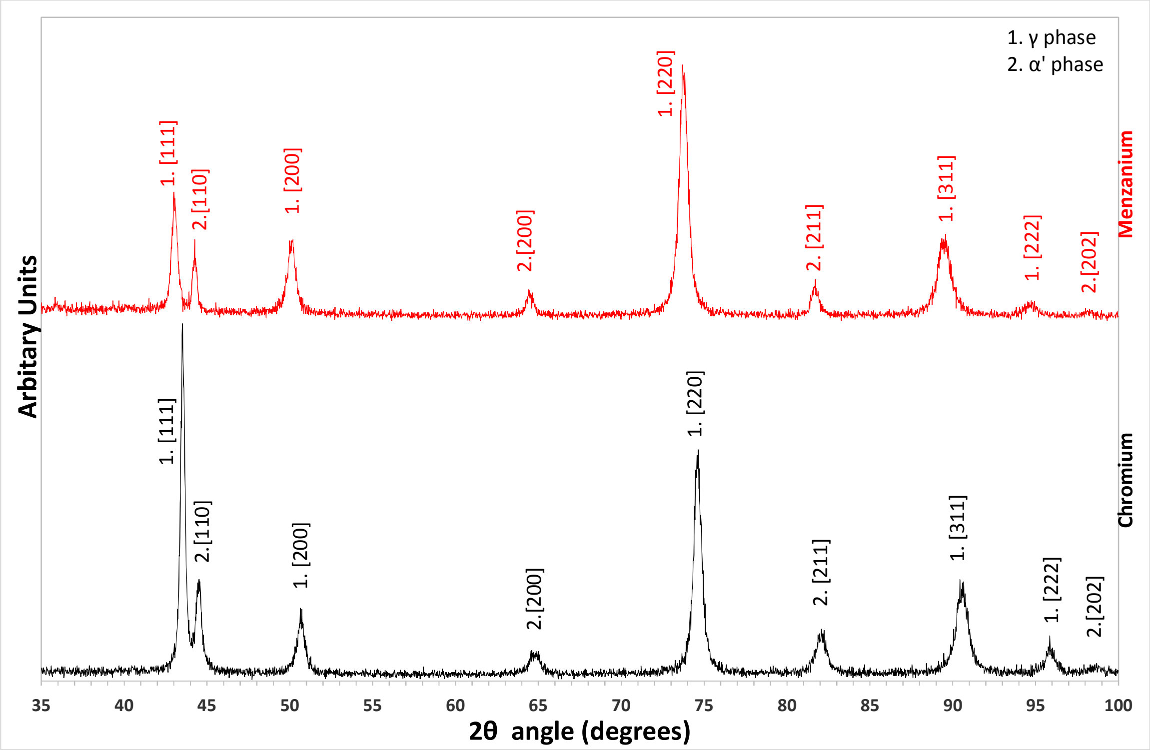

Figure 6. Indexed XRD patterns of Scheu-Dental Menzanium and Chromium wires

Table 3 summarizes the results of the electrochemical corrosion testing: the mean OCP, R_p, and I_{corr} values, as well as the significant differences resulting from the ANOVA/Tukey's Studentized Range (HSD) Test.

Table 3. Means with standard deviations for electrochemical measurements

	OCP (mV vs SCE)	**R_p (MΩ/cm^2)**	**I_{corr} (nA/cm^2)**
Acme Ni-Free	146 ± 40 ABC	55.1 ± 21.5 A	24 ± 9 B
Acme SS	105 ± 23 CD	8.4 ± 3.3 C	89 ± 16 B
Noninium	152 ± 24 AB	36.7 ± 11.9 B	25 ± 10 B
Remanium	156 ± 25 AB	31.5 ± 11.8 B	53 ± 20 B
Biosteel	97 ± 36 D	12.1 ± 6.6 C	173 ± 105 A
Leowire	175 ± 9 A	30.0 ± 8.3 B	57 ± 19 B
Menzanium	-38 ± 40 E	1.3 ± 0.1 C	201 ± 52 A
Chromium	115 ± 19 BCD	10.7 ± 2.5 C	203 ± 35 A

Tested in artificial saliva (Fusayama-Meyer solution)
SCE = Saturated Calomel Electrode
Wires with different letters denote significant differences ($p<0.05$) exist for each parameter (OCP, Rp, Icorr).

Figures 7-9 show a composite of the OCP graphs, polarization resistance curves, and potentiodynamic curves, respectively, of all wires.

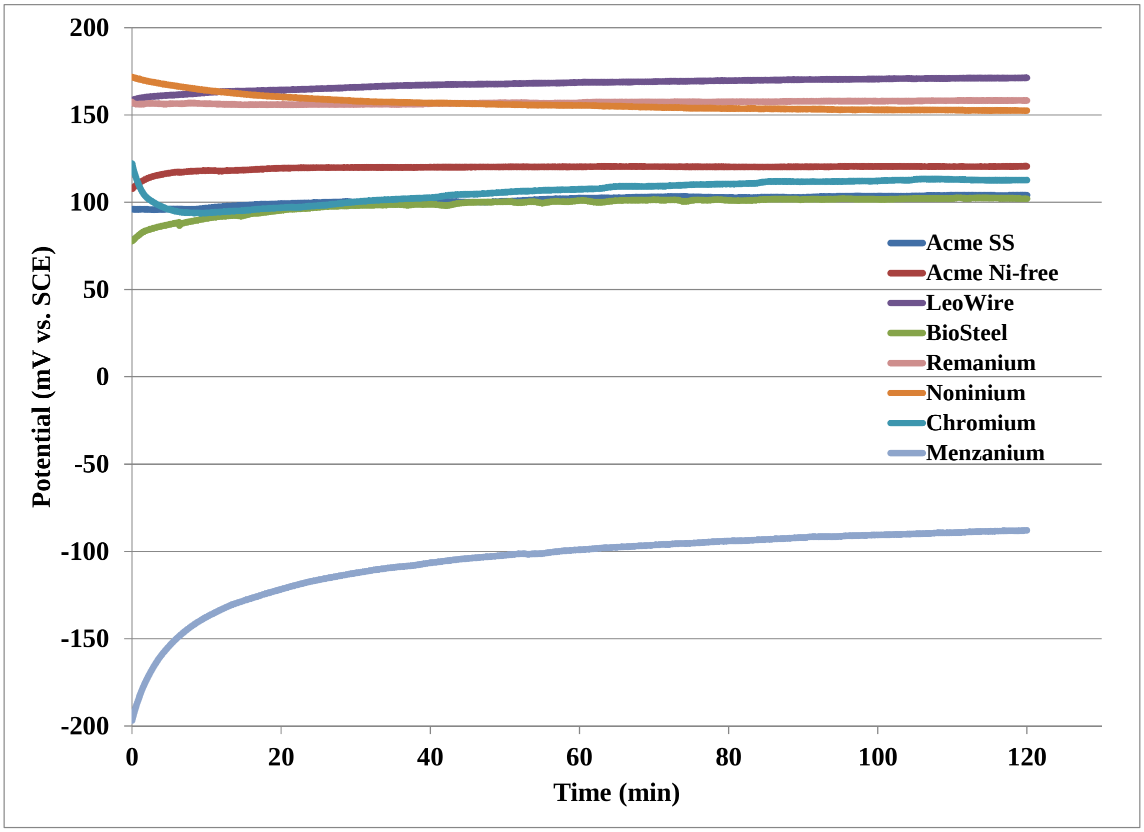

Figure 7. OCP curves for all wires

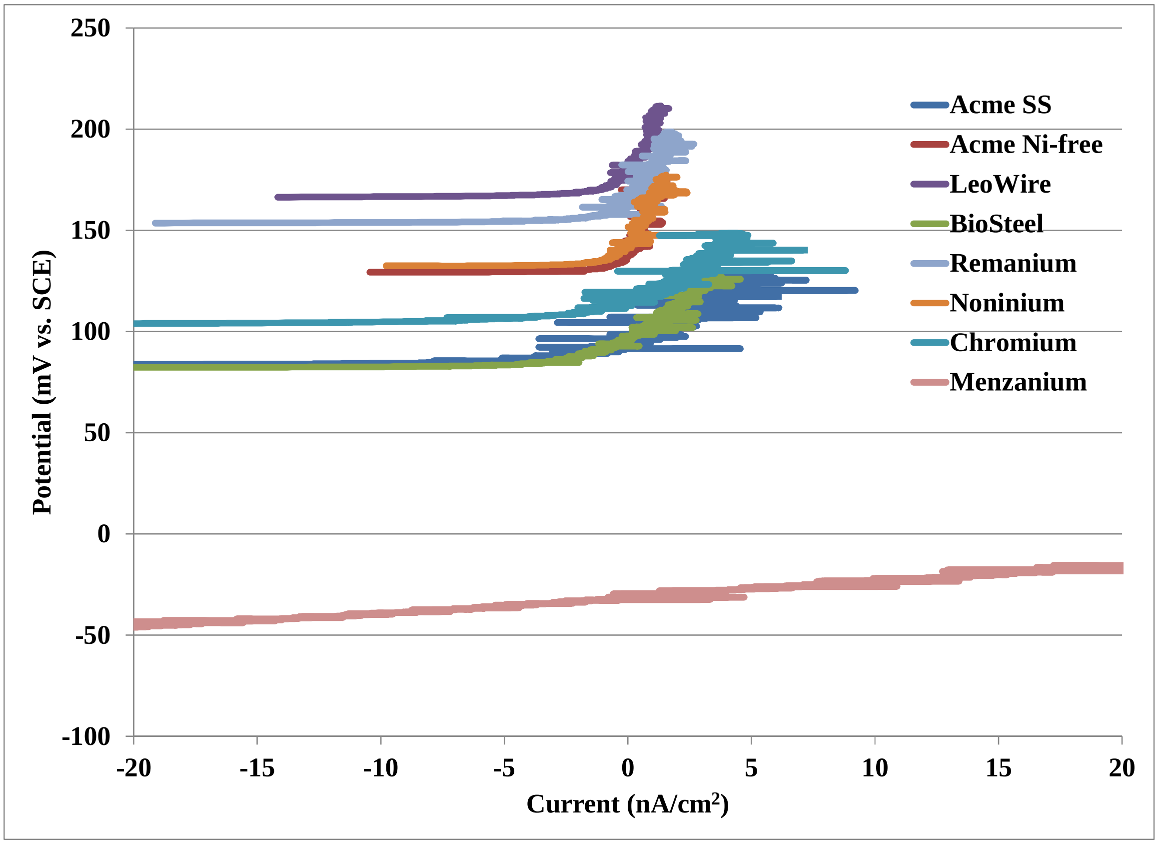

Figure 8. Polarization resistance curves for all wires

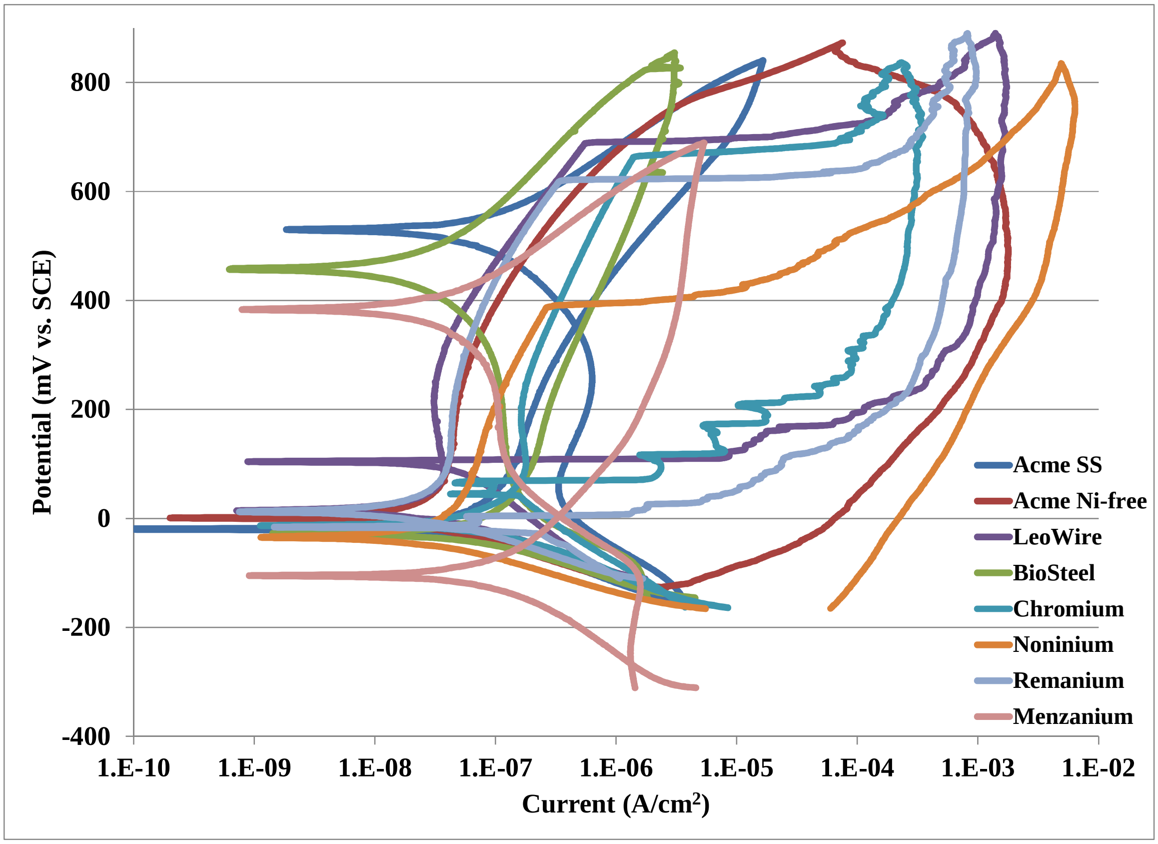

Figure 9. Potentiodynamic curves for all wires

CHAPTER 5
DISCUSSION

Nickel-free stainless steel wires can be an alternative to conventional stainless steel wires for orthodontic patients who are allergic to nickel. Because nickel is a key component to conventional austenitic stainless steel, the composition of nickel-free stainless steel must be altered to account for the absence (or very low amount) of nickel while still maintaining similar properties. The composition of four conventional stainless steel and four nickel-free stainless steel wires were determined using scanning electron microscopy with energy dispersive spectroscopy.

In this study, all of the nickel-free wires had an increased content of chromium, molybdenum, and manganese compared to the conventional stainless steel wires (Table 1). The difference in manganese content was the greatest difference with a range of 13.7-23.4% in the nickel-free wires and a range of 1.1-1.4% in the conventional stainless steel. Nickel serves to stabilize the austenite phase in stainless steel (Kusy, 1997; Eliades & Athanasiou, 2002). To substitute nickel as an austenite stabilizer, manganese, carbon, or nitrogen are typically used (Lai et al., 2012). Of the three alternatives, carbon is the least frequently used due to increased sensitization (Wataha, 2003; Lai et al., 2012) in the metallurgical sense. Sensitization from high carbon content leads to a decrease in corrosion resistance as the supply of chromium is depleted when carbide precipitates are formed with chromium and iron (Wataha, 2003). Based on this study, the manganese content is increased in the nickel-free wires to maintain the austenitic phase structure. All of the manufacturers list the presence of nitrogen in their nickel-free wires, with a range of 0.7-1.0%, and all but Biosteel are listed as having 0.1% or less of carbon (Table

2). Nitrogen and carbon are light elements and are not easily detectable by EDS; therefore, they are not listed in Table 1.

Another important observation is the detection of nickel (0.2%) in two of the nickel-free wires, Biosteel and Menzanium (Table 1). Most nickel-free stainless steels do have a small amount of nickel, but a significantly reduced amount (Rose et al., 1998; Schuster et al., 2004; Arndt et al., 2005; Verstrynge et al., 2006; Milheiro et al., 2012). All of the manufacturers listed the presence of nickel in their nickel-free wires as 0.2% nickel or less (Table 2).

Of the eight wires tested, only two demonstrated austenite as the only phase structure present, as determined by x-ray diffraction – the Acme Monaco Ultra Low Nickel stainless steel wire and Dentaurum’s Noninium wire (Figures 3 and 4). The other two nickel-free wires, Leone Biosteel and Scheu Menzanium, had austenite and martensite phase structures present. All of the conventional stainless steel wires had more than one phase structure present (Figures 3-6), which is consistent with previous investigations (Khier et al., 1988). Multiple phase structures may be present due to the effect of cold working and the presence of carbon (Khier et al., 1988; Wataha, 2003). An effect of the main substitution of manganese for nickel in the nickel-free wires is also apparent in the x-ray diffraction patterns. The austenite and martensite peaks are shifted to lower angles, which is consistent with the larger manganese substitution for nickel (the atomic radii of manganese is 140 pm while that of nickel is 135 pm).

Although there were significant differences among the wires for the three corrosion parameters (open circuit potential, polarization resistance, and corrosion current), there was not a general difference between nickel-free and conventional stainless steel wires (Table 3). Menzanium had the lowest OCP and the lowest polarization resistance, while Leowire had the highest OCP, and Acme Monaco’s Ultra Low Nickel stainless steel had the highest polarization resistance. Biosteel, Menzanium, and the stainless steel wire from Scheu had the highest corrosion current densities. The two wires from Dentaurum, Noninium and Remanium, were not significantly different for any of the parameters. The Leone Biosteel and Leowire were the only wire pair that was significantly different from each other for corrosion current density. Overall, the amount of corrosion does not appear to be different for the conventional stainless steel and nickel-free stainless steel wires.

CHAPTER 6
CONCLUSION

In order to maintain similar properties to conventional stainless steel wires, nickel-free stainless steel wires must account for the decreased amount of nickel by altering the composition of other elements. Manganese is significantly increased, but the content of chromium and molybdenum are also higher. Orthodontic stainless steel wires are mostly austenitic, but martensite may also be present in both conventional stainless steel and nickel-free stainless steel. There does not appear to be a difference in the corrosion properties of either type of stainless steel.

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