Corrosion of stainless steel, nickel-titanium, coated nickel-titanium, and titanium orthodontic wires

Hera Kim, DDS, MMSc; Jeffery W. Johnson, DDS, MS

Abstract: Orthodontic wires containing nickel have been implicated in allergic reactions. The potential for orthodontic wires to cause allergic reactions is related to the pattern and mode of corrosion with subsequent release of metal ions, such as nickel, into the oral cavity. The purpose of this study was to determine if there is a significant difference in the corrosive potential of stainless steel, nickel titanium, nitride-coated nickel titanium, epoxy-coated nickel titanium, and titanium orthodontic wires. At least two specimens of each wire were subjected to potentiostatic anodic dissolution in 0.9% NaCl solution with neutral pH at room temperature. Using a Wenking MP 95 potentiostat and an electrochemical corrosion cell, the breakdown potential of each wire was determined. Photographs were taken of the wire specimens using a scanning electron microscope, and surface changes were qualitatively evaluated. The breakdown potentials of stainless steel, two nickel titanium wires, nitride-coated nickel titanium, epoxy-coated nickel titanium, and titanium were 400 mV, 300 mV, 750 mV, 300 mV, 1800 mV, and >2000 mV, respectively. SEM photographs revealed that some nickel titanium and stainless steel wires were susceptible to pitting and localized corrosion. The results indicate that corrosion occurred readily in stainless steel. Variability in breakdown potential of nickel titanium alloy wires differed across vendors' wires. The nitride coating did not affect the corrosion of the alloy, but epoxy coating decreased corrosion. Titanium wires and epoxy-coated nickel titanium wires exhibited the least corrosive potential. For patients allergic to nickel, the use of titanium or epoxy-coated wires during orthodontic treatment is recommended.

Key Words: Corrosion, Potentiostatic anodic polarization, Orthodontic wires

Exposure to nickel has been shown to cause allergic reactions in many individuals.[1-15] Wires containing nickel are used routinely during orthodontic treatment. If these wires are susceptible to corrosion with subsequent nickel release, their use may elicit an allergic reaction in a patient with a true nickel allergy or contribute to the development of a nickel allergy.[13] The potential of an alloy to cause an allergic reaction is related to the pattern and mode of corrosion. Corrosion, which occurs in all base metals, is relatively high in nickel alloys compared with gold alloys.[9]

Electrolytic or electrochemical corrosion occurs in the oral cavity due, in part, to the wet environment.[16] A metal in an aqueous solution will be thermodynamically unstable if its tendency to pass from a solid state to an ionic form is associated with a decrease in energy. The direction of energy change is influenced by factors such as the metal itself, surface morphology and phase of the metal, galvanic coupling of dissimilar metals, solution composition, pH, and temperature. If the metal is unstable it may corrode, releasing metal ions into solution. This process will continue until equilibrium is reached, or until some occurrence impedes ion release. For example, a passivating film may form to prevent the metal from coming into contact with the solution. The surfaces of all metals react with oxygen to form a surface oxide layer, which inhibits an attacking substance from reaching the metal surface.[17] Corrosion of a metal that is covered by a protective film is dependent upon the properties of the film. Metals and alloys that rely on a passive film for corrosion resistance all share the property that, at sufficiently high potentials, the passive layer can be broken down and the metal or alloy will no longer be protected.[18] Metallic materials are not susceptible to corrosion as long as the surface oxide film is intact. But when the breakdown potential of an alloy is reached, the oxide layer dissolves and the onset of surface corrosion and pitting begins.[18,19,20]

Past corrosion studies have been conducted by simply observing the

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surface of an alloy before and after exposure to a corrosive environment and identifying visible evidence of corrosion, such as pitting.[9,21,22] Orthodontic appliances have been incubated in solutions with corrosive potential.[23-25] The solutions are subsequently tested for metal ions that leached out of the sample. Another type of corrosion testing is electrochemical and uses an applied potential to produce corrosion. The electrochemical technique used most often is potentiostatic anodic polarization.[26-45] Polarization measurements using potentiostatic techniques have been shown to be valuable in characterizing and quantifying active-passive systems. This technique is able to detect the transition of a system from a passive state to an active state or, in other words, to determine when corrosion begins.[34] Anodic polarization can fundamentally duplicate the electrochemistry of natural corrosion.[33,35] The natural conditions should be duplicated as closely as possible when using this process (for example, the physical state of the metal and the solution environment, including aerated or deaerated conditions).

The components needed to make potentiostatic anodic polarization measurements are an electrochemical corrosion cell, a data-acquisition device, and a potentiostat. The corrosion cell consists of a polarization cell and a reference cell connected by a salt bridge (Figure 1). The potentiostat functions by monitoring the potential between the working electrode and a reference electrode, and automatically alters the current between the working electrode and a counter electrode to maintain the desired potential.[36] The voltage is increased over time until the potential is sufficiently high to break down the passivating layer. This is referred to as the "critical" or "breakdown" potential (BP) and is accompanied by oxygen release from the surface film. Following the critical potential, the rate of metal dissolution is dramatically increased and a corresponding rise in current density is observed.[29]

Nickel titanium wires with epoxy and nitride coatings have recently been marketed. Nitride coatings were originally added to orthodontic wires to aid in surface hardening while epoxy electro-coating provided improved esthetics. Coated wires may be an important addition to the orthodontic armamentarium if corrosion can be inhibited and nickel ion release into the oral cavity prevented. The purposes of this study were to determine the corrosive potentials of various orthodontic wire alloys and to determine if epoxy or nitride coatings inhibit corrosion of the wire.

Materials and methods

The sample consisted of wires from three vendors ("A"-Company, San Diego, Calif; Ormco Co, Glendora, Calif; and FlexMedics, Minnetonka, Minn). Six 0.016 inch wires were tested, including "A"-Company's stainless steel, FlexMedics' nickel titanium (NiTi-A), Ormco's nickel titanium (NiTi-B), FlexMedics' nitride-coated nickel titanium, FlexMedics' epoxy-coated nickel titanium, and Ormco's titanium archwire. At least two specimens of each wire were tested. The percents by weight of chemical elements contained in the wire samples are listed in Table 1.

All preformed stainless steel, titanium, and uncoated nickel titanium archwires were used as received from the vendor; the preformed coated archwires were cut 15 mm from one distal end because the coating did not extend the full length of the wire.

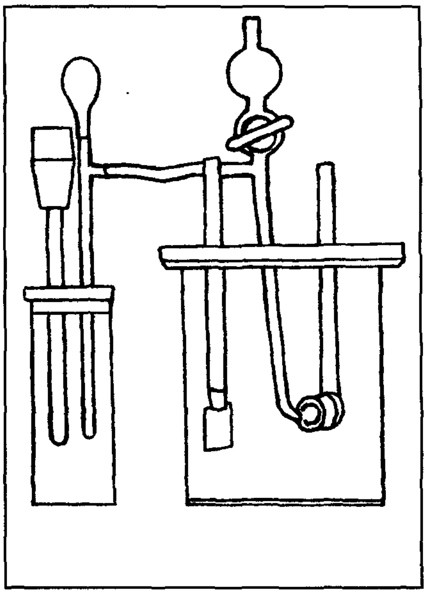

Figure 1
Schematic diagram of electrochemical corrosion cell

During anodic polarization, the potential of the test specimen was regulated with a Wenking MP 95 potentiostat (Bank Elektronik, Clausthal, Germany). The polarization current and potential were recorded using a computer, a screw board terminal (STP 37, Keithley Instruments, Tauton, Mass), a data-acquisition board (DAS 1602, Keithley Instruments), and a data-acquisition program (CPC-RP potentiostat software, Bank Elektronik).

An electrochemical corrosion cell (Bank Elektronik, Clausthal, Germany), which consisted of the polarization cell and reference cell, was used. The polarization cell held glass fixtures that received the working electrode (wire specimen), the auxiliary or counter electrode (platinum foil), and a Haber-Luggin probe. The reference cell held the reference electrode (Saturated Calomel Electrode, B 3410, Schott Gerate, Hofheim, Germany). The reference cell was connected to the polarization cell by way of a salt bridge consisting of tubing filled with 0.9% NaCl solution.

The accuracy of the potentiostat output was confirmed by constructing a dummy cell consisting of two 1.5 kOhm resistors. The potential dial was set at 1000 mV, and a digital voltmeter was used to take measurements from the current output and potential output terminals. The results from the voltmeter were compared with values received from the manufacturer to determine if they matched. The measurements recorded from the voltmeter were also compared with the current and potential measurements acquired by the data-acquisition computer program.

Each wire specimen was prepared by wiping it with 70% isopropyl alcohol to remove any surface debris. The wire was then placed into the working electrode fixture and adjusted so that 30 mm of wire was submerged in 900 ml of saline solution in the polarization cell. The tip of the Haber-Luggin probe was positioned approximately 2 mm from the working electrode. All electrodes were then connected to the potentiostat. The entire system was equilibrated at room temperature for 60 minutes. At 60 minutes, potential and current density measurements were started, and readings were taken every minute. At 65 minutes the potential was increased to 50 mV. The potential was increased 50 mV every 5 minutes until either the breakdown potential for the wire specimen or the 2000 mV potentiostat maximum was reached.

At least two specimens per wire were tested, as recommended by ASTM.[44] If the breakdown potential of the specimens varied significantly, a third specimen was tested. NiTi-A, NiTi-B, and nitride-coated NiTi required three runs each. The mean values of the runs were used to construct a potentiostatic anodic polarization curve for each wire. The breakdown potential for each wire was determined from the polarization curves.

Surfaces of the wires subjected to anodic dissolution were observed and compared with surfaces of the same wire not subjected to anodic dissolution using a scanning electron microscope. Photographs were taken of corroded and noncorroded areas of each wire for qualitative analyses.

Table 1
Composition (wt%) of alloys tested

	Ni	Cr	Fe	Ti	Sn	Zr	Mo
S.S. ("A"-Co.)	9%	18%	73%	——	——	——	——
NiTi (Ormco)	55%	——	——	45%	——	——	——
NiTi (FlexMedics)	55%	——	——	45%	——	——	——
TMA (Ormco)	——	——	——	78%	4.5%	6%	11.5%

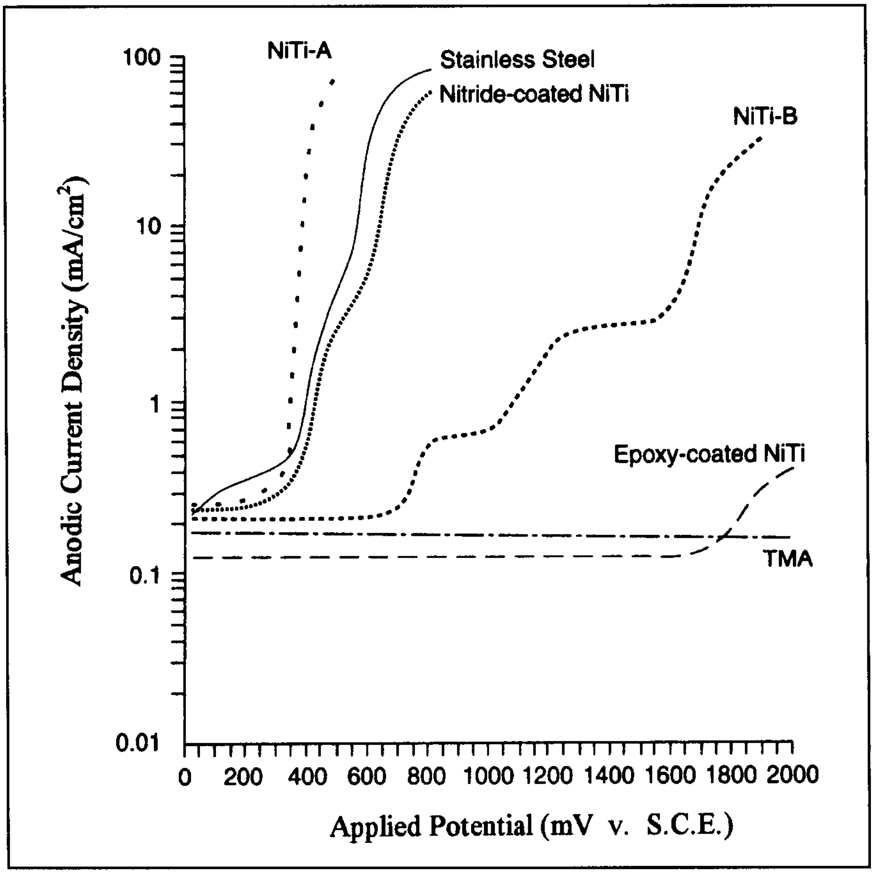

Figure 2
Applied potential-anodic current density variation of stainless steel, titanium, NiTi, nitride-coated NiTi, and epoxy-coated NiTi orthodontic wires

Results

The breakdown potential (BP) values for NiTi-A, nitride-coated NiTi, stainless steel, and NiTi-B wires were 300 mV, 300 mV, 400 mV, and 750 mV, respectively (Figure 2). Epoxy-coated NiTi wire had a breakdown potential of 1800 mV and a relatively small increase in current density. The breakdown potential of titanium wire could not be reached and the wire remained passive throughout the entire range of 2000 mV (Figure 2).

The results indicate that corrosion occurred readily in stainless steel and in some NiTi wires. The breakdown potentials of nickel-titanium wires seemed to vary between vendors. The nitride-coating did not affect corrosion of the wire alloy, but epoxy-coating decreased corrosion. The titanium and epoxy-coated nickel-titanium wires had the least corrosive potential, while NiTi-A wire had the greatest.

Microscopic examination of stainless steel, NiTi-A, and nitride-coated wires subjected to potentiostatic anodic polarization revealed extensive pitting and localized corrosion. All three wires showed significant changes in surface morphology (Figures 3A-B, 4A-B, and 5A-B) following anodic dissolution. NiTi-A wire that had not been subjected to potentiostatic anodic polarization had on its surface what appeared to be a crystallization phenomenon (Figure 4A). When examining the pitted regions of the corroded wire, these crystallization patterns appeared to extend into the wire (Figure 4B). Macroscopically, NiTi-B wire exhibited a color change from silver to dark gray after being subjected to potentiostatic anodic polarization, but no areas of pitting were discernible in the SEM photographs. The epoxy-coated NiTi wire and the titanium wire showed no detectable differences in surface morphology between specimens exposed to potentiostatic anodic polarization and those that were not. The observed surface changes were consistent within a given sample of wires.

Discussion

The breakdown potential indicates the point at which the oxide film of the alloy is broken down and dissolution of the alloy begins. A lower breakdown potential indicates higher susceptibility to corrosion. The greatest susceptibility to corrosion was observed in the NiTi-A and nitride-coated NiTi wires. Both these wires corroded similarly to the stainless steel wire. NiTi-B was less susceptible to corrosion. Epoxy-coated NiTi and titanium wires exhibited the least corrosive potential.

Overall, the breakdown potentials of the NiTi wires, with the exception of epoxy-coated NiTi, were lower than the comparable average values reported in previously published literature. Breakdown potentials for NiTi-A, NiTi-B, and nitride-coated NiTi wires (300 mV, 750 mV, and 300 mV, respectively) were lower than those reported for NiTi by Speck and Fraker[19] and Sedriks et al.[30]; their values ranged from 1100 mV to 1300 mV. In this study, stainless steel wires exhibited a breakdown potential (400 mV) that was higher than in previous reports (200mV).[19] The breakdown potential of titanium wire was not reached in this experiment and is consistent with most reports for titanium. Speck and Fraker reported a breakdown potential of 2000 mV for titanium when the potential applied went as high as 2500 mV.[19]

The differences in the BP values may be due to variations in material content of the metals, presence of surface defects and irregularities, presence of different phases of the metal, and differences in the corrosion cell environment, including aerated vs. deaerated conditions. In this study, the orthodontic wires were tested as received from the vendors and were not polished prior to anodic dissolution. Speck and Frakar and Sedriks et al. polished the surfaces of their samples in an attempt to reduce surface irregularities and imperfections.[19,30] Speck and Frakar reported that the surface finish of the alloy is the major influence on the corrosive resistance of nickel titanium. If surface defects and irregularities are present before a specimen is subjected to potentiostatic anodic polarization, the breakdown potential can decrease significantly, making it more prone to corrosion. When samples exhibited obvious surface irregularities prior to anodic polarization, the breakdown potential dropped as low as 430 mV for nickel titanium in previous studies. The BP values obtained for NiTi-A and nitride-coated nickel titanium wires are consistent with those obtained for nickel titanium with surface defects.

In this study, potentiostatic anodic polarization experiments were conducted using physiologic saline solution (0.9% NaCl). Earlier reports indicate that in vitro corrosion studies with physiologic saline solutions produced results comparable with those conducted in blood and other extracellular fluids, and similar results may be found in saliva.[26,28,33,37-43] This study was conducted without purging oxygen from solution in an attempt to more closely simulate the oral environment. Although Sedriks et al. showed no significant difference between breakdown potentials of specific metals tested in aerated solutions and those tested in deaerated solutions at room temperature, metal specimens tested in aerated solutions exhibited a faster rise in current density and ultimately, a higher current density.[30] Speck and Frakar reported slightly lower breakdown potentials for NiTi alloys at 37°C than Sedriks et al. observed at ambient room temperature (1100 mV vs. 1300 mV).[19,30] However, Speck and Frakar stated that the differences in the breakdown potentials of similar alloys are due primarily to the surface finishes of the metal samples, and that small temperature changes have limited influence on the breakdown potential of similar alloys.[19] Kerosuo et al. agree that the difference between room temperature and the more clinically relevant 37°C is small and is not likely to significantly affect the corrosive potential.[25]

Possible reasons for the differences in breakdown potentials of nickel titanium wires from different vendors may be related to trace elements in the alloys, presence of different phases of the metals, and varied surface conditions. Nickel titanium wires could also differ in the amounts and types of irregularities and internal stress, which can decrease corrosive resistance.[18]

The nitride-coated nickel titanium wire exhibited a mean breakdown potential that was not significantly greater than that of the uncoated nickel titanium from the same vendor, and exhibited extensive pitting of the wire. This result suggests that the nitride coating does not increase

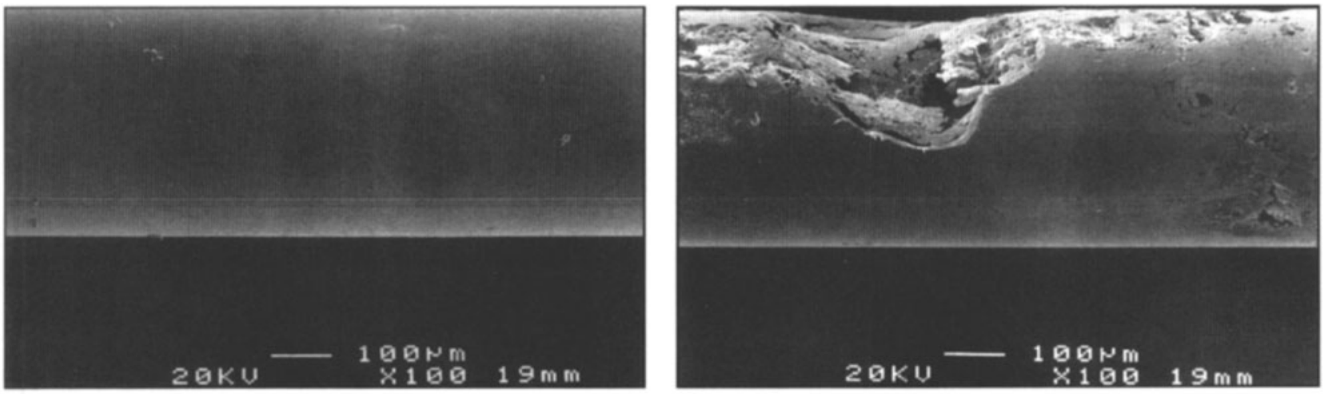

Figure 3A

Figure 3B

SEM photographs of stainless steel wires (A) not subjected to anodic polarization, and (B) subjected to anodic polarization

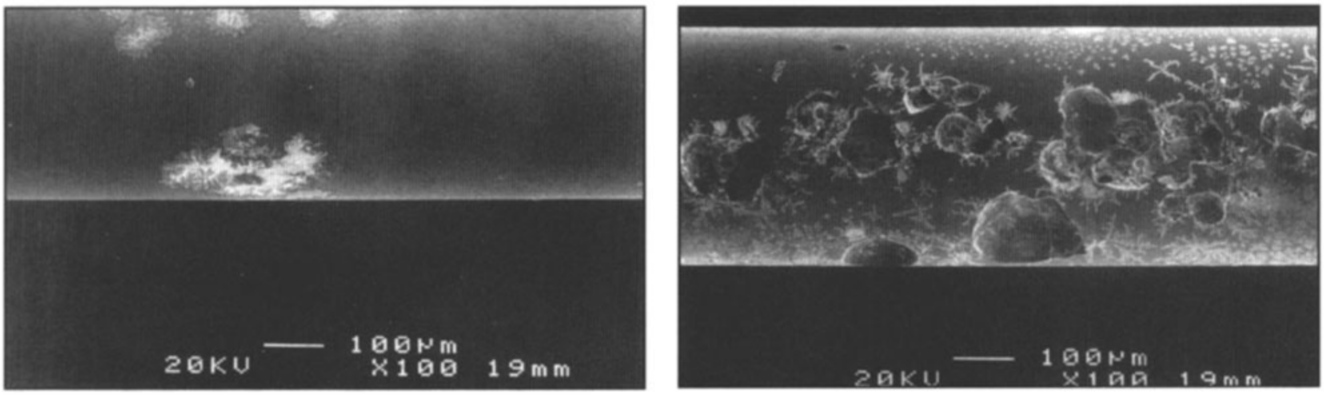

Figure 4A

Figure 4B

SEM photographs of NiTi-A wires (A) not subjected to anodic polarization, and (B) subjected to anodic polarization

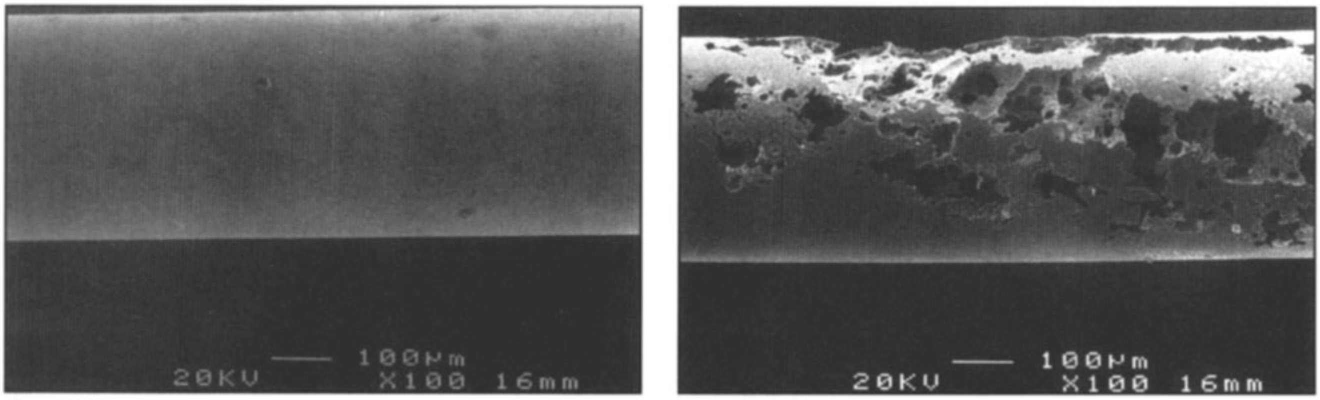

Figure 5A

Figure 5B

SEM photographs of nitride-coated NiTi wires (A) not subjected to anodic polarization, and (B) subjected to anodic polarization

the corrosive resistance of nickel titanium. However, the epoxy-coated nickel titanium wires showed significant corrosive resistance in this study. The BP of 1800 mV for the epoxy-coated nickel titanium was significantly greater than the BP for uncoated nickel titanium (300mV) from the same vendor. Corrosion of the epoxy-coated nickel titanium was probably due to the exposed metal at the cut end of the wire.

After examining the surface morphology of the corroded stainless steel and nickel titanium wires, Edie et al.[22] stated that the corrosive potentials of stainless steel and nickel titanium are not different. However, the present study indicates that there is a difference in BP, as well as more surface pitting and corrosion in stainless steel than in some nickel titanium wires. This result is consistent with most reports that stainless steel is more susceptible to corrosion than nickel titanium.[19,29,30,31]

Conclusion

Based on this study of corrosion susceptibility, titanium wire appears to be the most inert wire of those tested that can be used in a corrosive environment and is unlikely to release metal ions when used intraorally. It contains no nickel, making it an excellent choice for use in orthodontic patients with nickel sensitivity. If nickel titanium is to be used, epoxy-coating would protect it from the environment, thus lowering the corrosive potential and subsequent release of nickel. This study did not consider the loss of the coating that might occur during clinical use. If the epoxy coating can be maintained during orthodontic procedures, corrosion of the wire and release of metal ions into the oral cavity may be minimized during treatment.

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