Original Article

Corrosion Resistance of Different Nickel-Titanium Archwires in Acidic Fluoride-containing Artificial Saliva

Tzu-Hsin Lee[a]; Ta-Ko Huang[b]; Shu-Yuan Lin[c]; Li-Kai Chen[d]; Ming-Yung Chou[e]; Her-Hsiung Huang[f]

ABSTRACT

Objective: To test the hypothesis that different nickel-titanium (NiTi) archwires may have dissimilar corrosion resistance in a fluoride-containing oral environment.

Materials and Methods: Linear polarization test, a fast electrochemical technique, was used to evaluate the corrosion resistance, in terms of polarization resistance (R_p), of four different commercial NiTi archwires in artificial saliva (pH 6.5) with various NaF concentrations (0%, 0.01%, 0.1%, 0.25%, and 0.5%). Two-way analysis of variance was used to analyze R_p with the factors of archwire manufacturer and NaF concentration. Surface characterizations of archwires were analyzed using scanning electron microscopy, atomic force microscopy, and x-ray photoelectron spectroscopy.

Results: Both archwire manufacturer and NaF concentration had a significant influence on R_p of NiTi archwires. Different surface topography was present on the test NiTi archwires that contained the similar surface chemical structure (TiO_2 and trace NiO). The surface topography did not correspond to the difference in corrosion resistance of the NiTi archwires. Increasing the NaF concentration in artificial saliva resulted in a decrease in R_p, or corrosion resistance, of all test NiTi archwires. The NiTi archwires severely corroded and showed similar corrosion resistance in 0.5% NaF-containing environment.

Conclusions: Different NiTi archwires had dissimilar corrosion resistance in acidic fluoride-containing artificial saliva, which did not correspond to the variation in the surface topography of the archwires. The presence of fluoride in artificial saliva was detrimental to the corrosion resistance of the test NiTi archwires, especially at a 0.5% NaF concentration. (*Angle Orthod.* 2010;80:547–553.)

KEY WORDS: NiTi archwire; Corrosion resistance; Polarization resistance; Fluoride

[a] PhD Graduate Student, Institute of Medicine, Chung Shan Medical University; Orthodontics Specialist, Department of Dentistry, Chung Shan Medical University Hospital, Taichung, Taiwan.

[b] Adjunct Assistant Professor, College of Dental Medicine, Kaohsiung Medical University, Kaohsiung, Taiwan.

[c] Research Assistant, Department of Dentistry, National Yang-Ming University, Taipei, Taiwan.

[d] Department Head, Department of Dentistry, Taipei City Hospital, Taipei, Taiwan.

[e] Professor, Institute of Medicine, Chung Shan Medical University, Taichung, Taiwan.

[f] Professor, Department of Dentistry, National Yang-Ming University; Researcher, Taipei City Hospital, Taipei, Taiwan.

Corresponding author: Dr Her-Hsiung Huang, Department of Dentistry, National Yang-Ming University, No. 155, Sec. 2, Li-Nong St. Taipei 112, Taiwan
(e-mail: hhhuang@ym.edu.tw)

Accepted: September 2009. Submitted: March 2009.

INTRODUCTION

When using nickel-titanium (NiTi) archwire for dental orthodontic treatment, the possible danger associated with archwire corrosion derives from the biologically harmful effects of the released Ni ion.[1–3] Therefore, NiTi archwire with a good corrosion resistance is crucial to its biocompatibility. On the other hand, the surface corrosion of NiTi archwires may increase the friction that appears at the interface between the archwire and bracket, reducing the free sliding action during orthodontic treatment.

In dental applications, fluoride-containing commercial mouthwashes, toothpastes, and prophylactic gels are generally used to avoid dental caries or to reduce dental sensitivity. The fluoride ions degrade the protective TiO_2 film formed on Ti and Ti alloys.[4–8] Since the outermost surface of NiTi archwire contains mainly TiO_2 film with small amounts of NiO,[9] fluoride-enhanced corrosion of the NiTi archwire may occur. The corrosion behavior of a NiTi archwire in fluoride-containing mouthwashes (fluoride ion: a few hundred parts per million)[10,11] or prophylactic gels (fluoride ion: close to or more than 10,000 ppm)[12] has been investigated. However, information on the influence of fluoride concentration, contained in commercial fluorinated toothpastes (fluoride ion: a few hundred to a few thousand parts per million), on the corrosion resistance of commercial NiTi orthodontic archwires is still limited. Furthermore, NiTi archwires produced by various manufacturers may have different corrosion resistances in the oral environment. In the previous study,[13] the corrosion resistance of different Ni-Ti archwires in fluoride-free acidic artificial saliva is different. However, related knowledge concerning the effect of fluoride concentration on the comprehensive difference in corrosion resistance of commercial NiTi archwires from various manufacturers still requires further investigation.

The hypothesis is that different brands of NiTi archwires may have dissimilar corrosion resistance in oral environments with different fluoride concentrations. In the present investigation, we studied the dissimilarity of the corrosion resistance of commercial NiTi archwires produced by different manufacturers. Experiments were performed in acidic artificial saliva with different NaF concentrations, simulating commercial fluoride-containing toothpastes. The surface characterizations of different NiTi archwires were compared and correlated with the corrosion resistance.

MATERIALS AND METHODS

Four different as-received commercial round (Ø: 0.016-inch) NiTi dental orthodontic archwires containing approximately equi-atomic Ni and Ti elements were used in this study. These four types of archwires were designated as follows: Dent (Rematitan® Lite, Dentaurum, Ispringen, Germany), Ormco (Ni-Ti®, Ormco, Glendora, Calif), RMO (Orthonol® Nickel-Titanium Wire, RMO Inc, Denver, Colo), and SY (NiTi Wire, Shin-Ya Co, Taipei, Taiwan).

A scanning electron microscope (ABT-150S, Topcon, Tokyo, Japan) was used to observe the surface morphologies of the archwires. The three-dimensional surface roughness (R_a) of the archwires was evaluated using atomic force microscopy (Nanoscope III, Digital Instruments Inc, Santa Barbara, Calif). The R_a represents the arithmetical mean of the absolute values of the scanned surface profile (50 μm $\times$ 50 μm). The outermost surface chemical structures of the archwires were assessed using x-ray photoelectron spectroscopy (XPS) (ESCALAB 210, VG Scientific Ltd, East Grinstead, UK). For the surface characterization analysis of each NiTi archwire group, the sample size was three. These three samples had identical material batch numbers.

A potentiostat (AUTOLAB PGSTAT 30, Eco Chemie BV, Utrecht, The Netherlands) was used to perform the linear polarization test,[14] a fast and nearly nondestructive electrochemical technique. NiTi archwires were used as working electrodes. A saturated calomel electrode and platinum sheet were used as the reference electrode and counter electrode, respectively. Modified Fusayama artificial saliva with a pH of 6.5 at 37°C was used as the corrosion test electrolyte[13]; the artificial saliva consisted of NaCl (400 mg/L), KCl (400 mg/L), $CaCl_2 \cdot 2H_2O$ (795 mg/L), $NaH_2PO4 \cdot H_2O$ (690 mg/L), KSCN (300 mg/L), $Na_2S \cdot 9H_2O$ (5 mg/L), and urea (1000 mg/L). To evaluate the effect of fluoride concentration on the corrosion resistance of commercial NiTi archwires, different amounts of NaF were added to the artificial saliva to prepare 0.01%, 0.1%, 0.25%, and 0.5% NaF concentrations, simulating the fluoride concentrations contained in commercial fluoridated toothpastes. The fluoride ion concentrations in the artificial saliva containing 0.01%, 0.1%, 0.25%, and 0.5% NaF were measured using a fluoride electrode (No. 27502-19, Cole-Parmer Instrument Co, Vernon Hills, NY), which revealed concentrations of about 46 ppm, 461 ppm, 1130 ppm, and 2250 ppm, respectively.

The linear polarization tests, in terms of linear polarization curve measurements, of the NiTi archwires were carried out after dipping the archwires into the test electrolyte for 2 hours. Note that the open circuit potential of the NiTi archwires in all test electrolytes could reach stable value in about 1 hour. The linear polarization curves were measured from -10 mV to $+10$ mV (vs corrosion potential), with a scan rate of 0.1 mV/s. The polarization resistance (R_p [Ω cm^2]), which is inversely proportional to the corrosion rate, is defined as the slope of the potential (V) vs the current density (A cm^{-2}) near corrosion potential in the linear polarization curves.[14] The R_p value was statistically analyzed using two-way analysis of variance for analyzing the variable factors of the archwire manufacturer and NaF concentration (α = 0.05). For the corrosion test of each NiTi archwire group, the sample size was five. These five samples had identical material batch numbers.

RESULTS

Figure 1 shows the scanning electron microscope images of the test as-received commercial NiTi archwires. Surface defects produced during the manufacturing process were noticeable on Ormco and SY archwires, while some small surface scratches created during the manufacturing process were observed on Dent and RMO archwires. The scanning electron microscope images in Figure 1 actually represented the surface textures of the test NiTi archwires. Figure 2 and Table 1, respectively, show

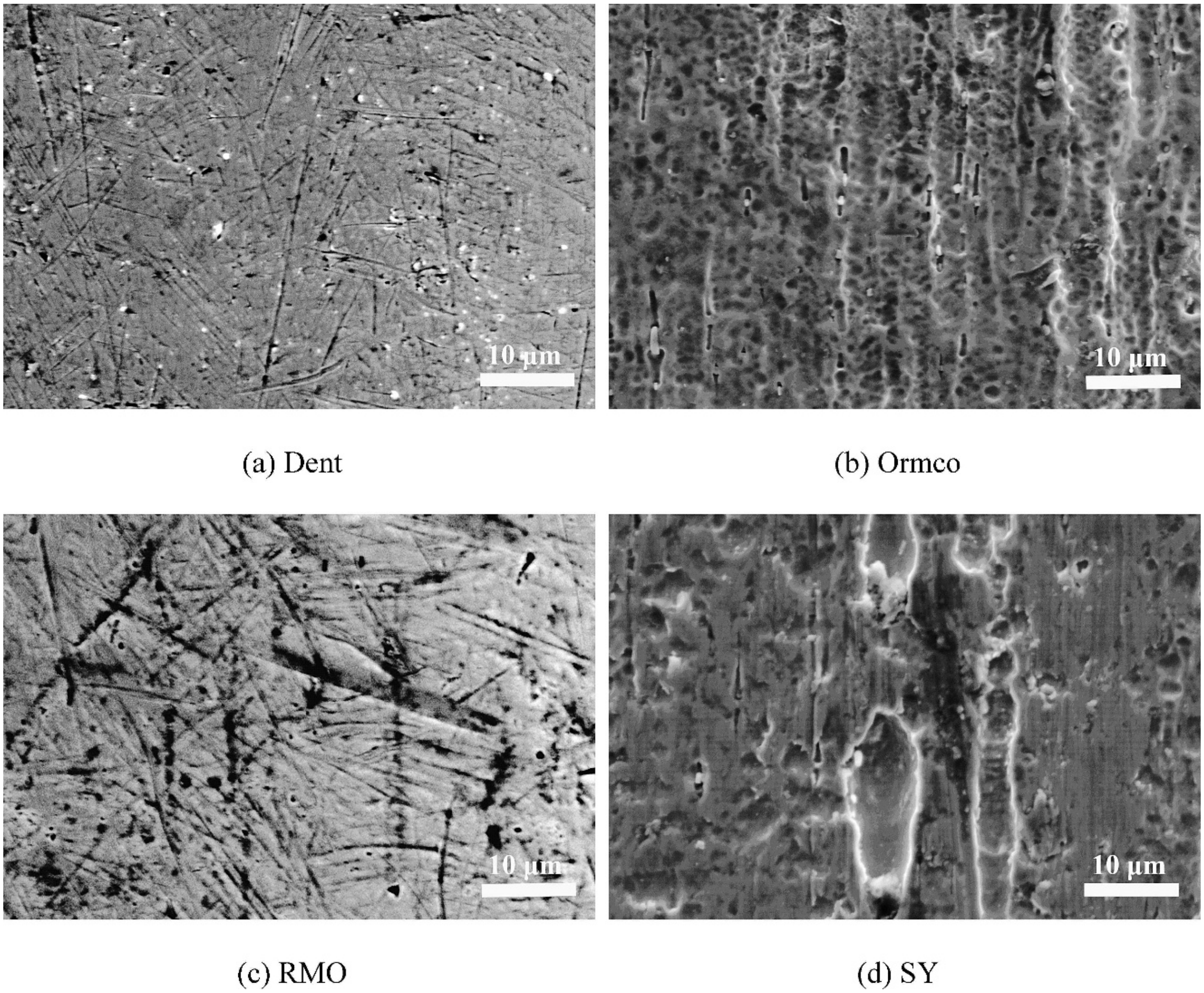

Figure 1. Scanning electron microscope (SEM) observations of the as-received commercial nickel-titanium (NiTi) archwires from different manufacturers (Dent, Ormco, RMO, and SY).

the atomic force microscopy images and the corresponding surface roughness (R_a: μm) of the test as-received commercial NiTi archwires. A rougher surface was visible on Ormco (R_a: 1.27 μm) and SY (R_a: 0.90 μm) archwires, whereas RMO archwire exhibited the least surface roughness (R_a: 0.19 μm). Figure 3 shows the XPS surface analysis results of the commercial NiTi archwire (Ormco) before (as-received condition) and after the corrosion test in 0.5% NaF–containing artificial saliva. Results show that the outermost surface chemical structure of the passive film on the as-received Ormco archwire contained mainly TiO_2, with trace amounts of NiO. After the corrosion test in 0.5% NaF–containing solution, the Ti-F complex compound (Na_2TiF_6) could be detected on the Ormco archwire along with the those oxides detected on the as-received archwires. Similar XPS analysis results mentioned above were also obtained for the other three archwires (Dent, RMO, and SY).

Table 2 shows the R_p values, obtained from the linear polarization tests, of the NiTi archwires from different manufacturers. Results of two-way analysis of variance showed that the archwire manufacturer and NaF concentration had a statistically significant influence on the R_p value (archwire manufacture: $P < .01$; NaF concentration: $P < .001$). Increasing the NaF concentration resulted in a decrease in the R_p values of NiTi archwires, regardless of archwire manufacturer. The R_p values of NiTi archwires decreased from 45.5–91.2 $\times 10^3$ to 14.2–31.6 $\times 10^3$ Ω cm^2 when the NaF concentration changed from 0% to 0.25% (fluoride ion: from 0 to 1130 ppm): the Ormco archwire had the highest R_p value and for the most part the SY archwire had the lowest R_p value under the same NaF concentration. In artificial saliva with a high 0.5% NaF concentration (fluoride ion: 2250 ppm), the R_p values of all test NiTi archwires significantly decreased to 1.2–2.2 $\times 10^3$ Ω cm^2, and no significant difference in R_p was

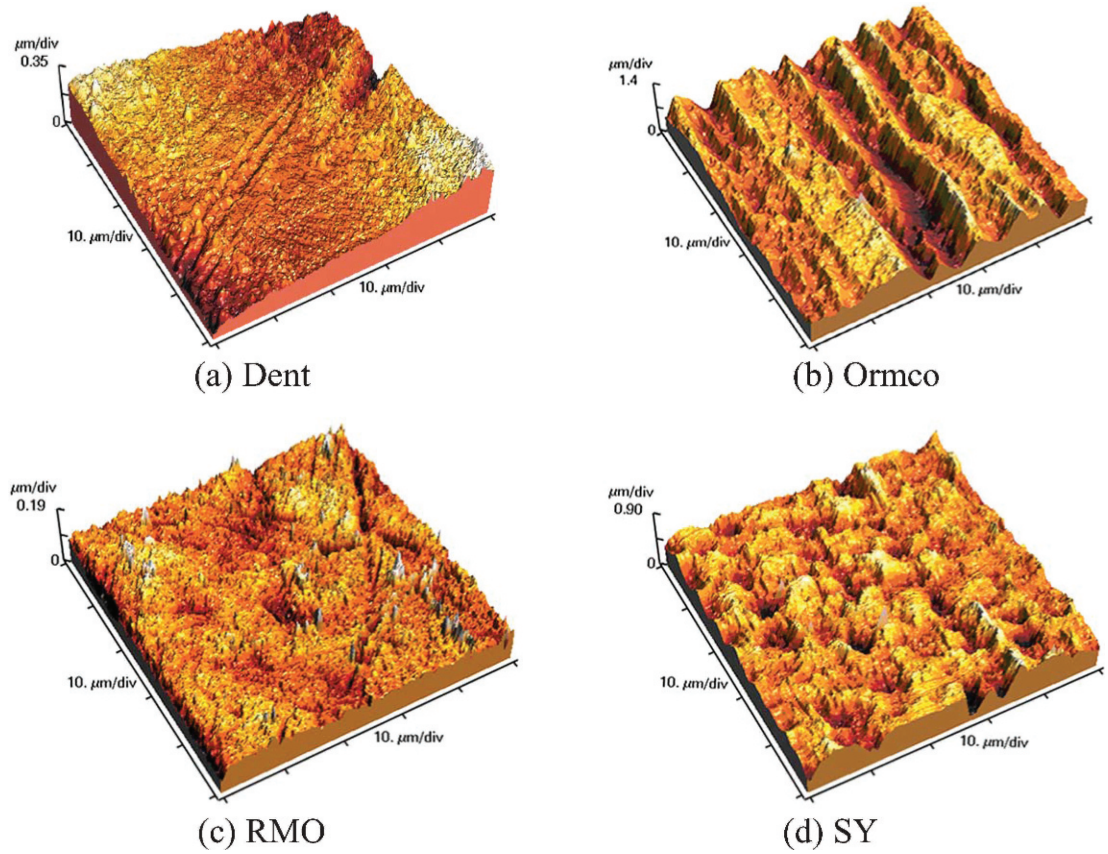

Figure 2. Atomic force microscope (AFM) observations of the as-received commercial nickel-titanium (NiTi) archwires from different manufacturers (Dent, Ormco, RMO, and SY).

present among the four types of archwires at this high NaF concentration of 0.5%.

DISCUSSION

In this study, the R_p value could be rapidly calculated from the linear polarization test (selected as a nondestructive and rapid electrochemical technique) and used as a parameter for corrosion resistance evaluation of NiTi archwires. Although the XPS analysis results revealed that the surface chemical structure of the passive film on all test NiTi archwires was similar, a statistically significant difference in R_p, or corrosion resistance, was found among the NiTi archwires from different manufacturers ($P < .01$), regardless of the NaF concentration (0%–0.25%) in artificial saliva. The significant difference in R_p could be due to the variation in surface characterizations.

A previous study[15] showed that the surface roughness of orthodontic archwires ought to be taken as an important indicator of the trend toward archwires' corrosion resistance. The surface defects on NiTi orthodontic archwire produced during the manufacturing procedure can be the probable locations for corrosion occurrence.[16] However, in this study, the Ormco archwire (with the notable surface defects and highest surface roughness shown in Figure 1 and Table 1) did not exhibit a lower R_p value or a lower corrosion resistance, regardless of the NaF concentration in artificial saliva (Table 2). This was similar to the results reported by the previous studies, which showed that a NiTi archwire with a rougher surface does not exhibit greater metal ion release[17] or lower corrosion resistance[13] in fluoride-free acidic artificial saliva. In this study, the difference in R_p among the four types of NiTi archwires with the same surface passive film was believed to be related to the varying surface residual stress produced during the different manufacturing procedures rather than to the notable surface defects and/or surface roughness.

Table 1. Mean Values of Surface Roughness (R_a [μm]), Derived from Atomic Force Microscopy (AFM) Images, of the As-Received Commercial Nickel-Titanium (NiTi) Archwires from Different Manufacturers (Dent, Ormco, RMO, and SY)

	Dent	Ormco	RMO	SY
R_a	0.36 (0.09)[a]	1.27 (0.37)	0.19 (0.11)	0.90 (0.29)

[a] Standard deviations are given in parentheses.

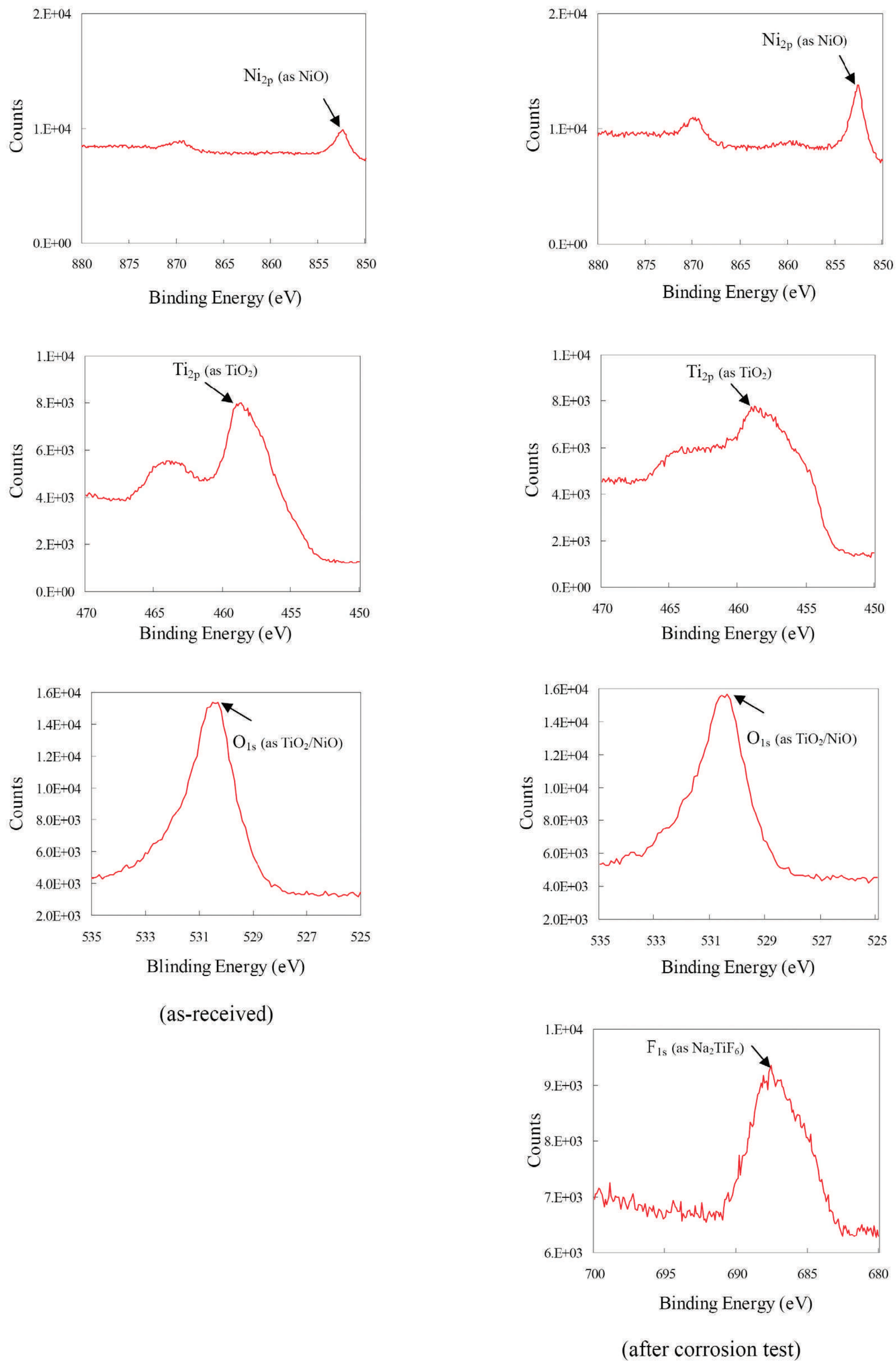

Figure 3. X-ray photoelectron spectroscopy (XPS) surface analysis results of the commercial nickel-titanium (NiTi) archwire (Ormco) before (as-received condition) and after corrosion test in 0.5% NaF-containing artificial saliva.

Table 2. Mean Values of Polarization Resistance (R_p [Ω cm^2]), Obtained from Linear Polarization Tests in Acidic Artificial Saliva with Different NaF Concentrations, of the As-Received Commercial Nickel-Titanium (NiTi) Archwires from Different Manufacturers (Dent, Ormco, RMO, and SY)

	NaF, %				
Archwire	0	0.01	0.1	0.25	0.5
Dent	53.0×10^3 (1877)[a]	42.9×10^3 (2187)	31.3×10^3 (1933)	14.2×10^3 (1323)	1.2×10^3 (641)
Ormco	91.2×10^3 (1401)	83.5×10^3 (1138)	67.9×10^3 (1519)	31.6×10^3 (976)	1.6×10^3 (851)
RMO	62.6×10^3 (915)	51.0×10^3 (898)	45.8×10^3 (788)	22.0×10^3 (794)	2.2×10^3 (496)
SY	45.5×10^3 (1156)	41.8×10^3 (1057)	29.6×10^3 (595)	21.3×10^3 (989)	1.5×10^3 (591)

[a] Standard deviations are given in parentheses.

It is well recognized that a metal's biocompatibility is related to the protectiveness of its surface passive film.[18,19] NiTi archwire with a good long-term corrosion resistance, namely with a lastingly protective TiO_2-based passive film, in an acidic oral environment is necessary to its biocompatibility. Among the test NiTi archwires in this study, Ormco archwire showed the highest R_p (31.6–91.2 $\times$ 10^3 Ω cm^2) in the acidic artificial saliva with lower NaF ($\leq$0.25%) concentration (fluoride ion $\leq$ 1130 ppm). Therefore, in terms of corrosion resistance, this Ormco archwire was suggested as a potential candidate among the test NiTi archwires for dental orthodontic treatment in low–fluoride-containing environment. However, regardless of the archwire manufacturer, all test NiTi archwires showed a significantly decreased R_p value of about 1.2–2.2 $\times$ 10^3 Ω cm^2 in high–0.5% NaF-containing environment (fluoride ion: 2250 ppm). This indicated that the surface passive film on all test NiTi archwires was severely damaged by fluoride ions when the NaF concentration in artificial saliva increased to 0.5%.

It has been reported[6,7] that the protectiveness of TiO_2 formed on Ti and Ti-6Al-4V alloy is degraded by fluoride ions when the NaF concentration exceeds 0.1% (fluoride ion: close to 500 ppm) via the formation of a Ti-F complex compound. Previous studies[10,11] have shown that a NiTi orthodontic archwire in commercially available fluoride mouthwashes (fluoride ion: close to 250 ppm) can corrode. In this study, the corrosion resistance, in terms of R_p, of the test NiTi archwires decreased as the NaF concentration increased (Table 2), regardless of archwire manufacturer. In other words, the protectiveness of the TiO_2-based passive film on the four types of NiTi archwires was harmfully influenced by the presence of NaF (fluoride ions: 46 ppm, 461 ppm, 1130 ppm, and 2250 ppm) in the acidic artificial saliva, especially at a higher fluoride concentration of 2250 ppm, through the formation of Ti-F complex compound Na_2TiF_6 (Figure 3).

In acidic fluoride-free artificial saliva, the R_p value for Ti with a surface chemical structure composed of TiO_2 is approximately 10^6 Ω cm^2,[20] whereas the R_p value for Ti-6Al-4V with a surface structure composed primarily of TiO_2 is around 4.5×10^4 Ω cm^2.[7] In this study, the R_p values of the test NiTi archwires in low–NaF ($\leq$0.1%)-containing artificial saliva ranged between 3.1×10^4 Ω cm^2 and 9.1×10^4 Ω cm^2. These values were lower than that of Ti but close to or greater than that of Ti-6Al-4V alloy in fluoride-free artificial saliva, as mentioned above. Based on the above-mentioned results, the corrosion resistance of the four types of NiTi archwires investigated in the low–NaF ($\leq$0.01%)-containing acidic oral environment could be acceptable, despite variance in the corrosion resistance among the test NiTi archwires. Note that the R_p values for the test NiTi archwires decreased to about 1.2–2.2 $\times$ 10^3 Ω cm^2 when tested in a high–0.5% NaF-containing environment. This was expected to result in greater metal ion release and enlarged friction between the archwire and bracket as a result of increased archwire surface roughness.

In this study, the R_p values were measured after exposing the archwires to the fluoride-containing test electrolytes for 2 hours. This simulated the in vivo corrosion resistance of the archwires when the residual fluorinated toothpastes interacted with the archwires for 2 hours after tooth brushing. It was expected that the in vivo corrosion resistance of the archwires in oral environments might decrease if the highly fluorinated toothpastes were used and/or the exposure time of archwires to residual fluorinated toothpastes was prolonged. Therefore, complete removal of residual high-fluorinated toothpastes from the crevice between archwire and bracket during tooth brushing is required. Furthermore, the repair of the protectiveness of surface oxide film on the NiTi archwires might occur after full removal of residual fluorinated toothpastes by mechanical tooth brushing. However, further investigation is required to determine if there is a critical concentration of residual fluoride ions.

It should be noted that in this study the 0.5% NaF concentration (fluoride ions: 2250 ppm) offered the worst situation in terms of destroying the protectiveness of passive film on the test NiTi archwires. Nevertheless, certain dental fluoride gels may contain fluoride ions at a concentration of greater than 10^4 ppm, which is expected to damage the TiO_2-based passive film on NiTi archwires. Thus, careful and precise post–tooth brushing is strongly suggested. However, in high–fluoride (0.5% NaF)-containing artificial saliva, the corrosion resistance of all test NiTi archwires notably decreased, and no significant difference in polarization resistance was present among the archwires. Therefore, it is suggested that cleaning away the residual high-fluorinated toothpastes from the crevice between the NiTi archwire and bracket during tooth brushing is critical.

CONCLUSIONS

- The archwire manufacturer and NaF concentration had a statistically significant influence on the corrosion resistance, in terms of polarization resistance, of the four different kinds of commercial NiTi orthodontic archwires in acidic fluoride-containing artificial saliva.
- The surface topography of the commercial NiTi archwires with identical surface chemical structures, TiO_2, and small amounts of NiO, did not correspond to the variation in corrosion resistance in fluoride-containing artificial saliva.

ACKNOWLEDGMENTS

The authors would like to thank the National Science Council, Taiwan (grant NSC 96-2628-B-010-032-MY3), and Taipei City Hospital (grant 95004-62-169) for financial support.

REFERENCES

1. Brantley WA, Eliades T. *Orthodontic Materials: Scientific and Clinical Aspects*. Stuttgart, Germany: Thieme; 2001:77–104.
2. El Medawar L, Rocher P, Hornez JC, Traisnel M, Breme J, Hildebrand HF. Electrochemical and cytocompatibility assessment of NiTiNOL memory shape alloy for orthodontic use. *Biomol Eng*. 2002;19:153–160.
3. Es-Souni M, Es-Souni M, Fischer-Brandies H. On the properties of two binary NiTi shape memory alloys. Effects of surface finish on the corrosion behaviour and in vitro biocompatibility. *Biomaterials*. 2002;23:2887–2894.
4. Nakagawa M, Matsuya S, Udoh K. Effects of fluoride and dissolved oxygen concentrations on the corrosion behavior of pure titanium and titanium alloys. *Dent Mater J*. 2002;21:83–92.
5. Schiff N, Grosgogeat B, Lissac M, Dalard F. Influence of fluoride content and pH on the corrosion resistance of titanium and its alloys. *Biomaterials*. 2002;23:1995–2002.
6. Huang HH. Effects of fluoride concentration and elastic tensile strain on the corrosion resistance of commercially pure titanium. *Biomaterials*. 2002;23:59–63.
7. Huang HH. Effect of fluoride and albumin concentration on the corrosion behavior of Ti-6A1-4V alloy. *Biomaterials*. 2003;24:275–282.
8. Huang HH, Lee TH. Electrochemical impedance spectroscopy study of Ti-6A1-4V alloy in artificial saliva with fluoride and/or albumin. *Dent Mater*. 2005;21:749–755.
9. Huang HH. Corrosion resistance of stressed NiTi and stainless steel orthodontic wires in acid artificial saliva. *J Biomed Mater Res A*. 2003;66A:829–839.
10. Schiff N, Grosgogeat B, Lissac M, Dalard F. Influence of fluoridated mouthwashes on corrosion resistance of orthodontics wires. *Biomaterials*. 2004;25:4535–4542.
11. Schiff N, Boinet M, Morgon L, Lissac M, Dalard F, Grosgogeat B. Galvanic corrosion between orthodontic wires and brackets in fluoride mouthwashes. *Eur J Orthod*. 2006;28:298–304.
12. Watanabe I, Watanabe E. Surface changes induced by fluoride prophylactic agents on titanium-based orthodontic wires. *Am J Orthod Dentofacial Orthop*. 2003;123:653–656.
13. Huang HH. Variation in corrosion resistance of NiTi wires from different manufacturers. *Angle Orthod*. 2005;75:569–573.
14. Jones DA. *Principles and Prevention of Corrosion*. 2nd ed. Upper Saddle River, NJ: Prentice-Hall Inc; 1996:143–167.
15. Widu F, Drescher D, Junker R, Bourauel C. Corrosion and biocompatibility of orthodontic wires. *J Mater Sci Mater Med*. 1999;10:275–281.
16. Oshida Y, Sachdeva RCL, Miyazaki S. Microanalytical characterization and surface modification of TiNi orthodontic archwires. *Biomed Mater Eng*. 1992;2:51–69.
17. Huang HH, Chiu YH, Lee TH, Wu SC, Yang HY, Su KH, Hsu CC. Ion release from NiTi orthodontic wires in artificial saliva with various acidities. *Biomaterials*. 2003;24:3585–3592.
18. Baker MA, Assis SL, Higa OZ, Costa I. Nanocomposite hydroxyapatite formation on a Ti-13Nb-13Zr alloy exposed in a MEM cell culture medium and the effect of H_2O_2 addition. *Acta Biomater*. 2009;5:63–75.
19. Yoo YR, Jang SG, Oh KT, Kim JG, Kim YS. Influences of passivating elements on the corrosion and biocompatibility of super stainless steels. *J Biomed Mater Res B Appl Biomater*. 2008;86:310–320.
20. Huang HH, Hsu CH, He JL, Pan SJ, Chen CC. Corrosion and cell adhesion behavior of TiN-coated and ion-nitrided titanium for dental application. *Appl Surf Sci*. 2005;244:252–256.