

In vitro surface corrosion of stainless steel and NiTi orthodontic appliances

Ji-Soo Shin

DDS, PhD
Private Practice, Shin Ji-Soo
Dental Clinic
Seoul
Korea

Keun-Taek Oh

PhD
Research Institute of Dental Materials
College of Dentistry, Yonsei University
Seoul
Korea

Chung-Ju Hwang

DDS, PhD
Professor, Department of Orthodontics
College of Dentistry, Yonsei University
Seoul
Korea

Simulated fixed orthodontic appliances were constructed, immersed and incubated in artificial saliva for periods up to three months. Two types of stainless steel archwires and two types of NiTi wires were used. The surface corrosion of the archwires was determined macroscopically, with scanning electron microscopy, and with spectrophotometry. The deposits on the wires were identified with X-ray diffraction. Uniform corrosion was observed on stainless steel wires, and a slight colour change was detected on the NiTi wires beneath stainless steel ligatures. The corrosion product on the stainless steel wires increased with immersion time, and the surface oxide films were easily detached from the underlying matrix. Crevice corrosion was observed under deposits of oxide, and at the interface between bracket and band. Such corrosion may weaken a wire or weld leading to fracture. In contrast, the NiTi archwires did not corrode, and there was no significant difference in surface morphology. The stainless steel archwires showed a significant loss of reflectance after heat treatment and immersion in artificial saliva. The NiTi archwires had the same reflectance before and after the immersion test. NiTi archwires are significantly more stable and resistant to corrosion than stainless steel archwires. Aust Orthod J 2003; 19: 13–18

Introduction

Corrosion is an electrochemical reaction between a metal and its environment resulting in the formation of chemical compounds.¹ Orthodontic bands, brackets, ligatures, springs and archwires are liable to corrosion because they are immersed in an electrolyte – saliva, and factors such as warm oral temperatures, the presence of plaque, some foods and beverages, and systemic and oral health conditions provide a corrosive environment. Oxygen, the third requirement for corrosion to occur, is present in abundant quantities in the mouth. Processes such as finishing and polishing, heat treatment and cold working may alter the chemical and physical properties of the metallic components of appliances leading to loss of the protective film and corrosion.^{2–6}

Destruction of a metal by corrosion can occur through the loss of metal ions or by progressive dissolution of the surface film. As a rule, corrosion distributed uniformly over a metal surface is less destructive than localized forms of attack, which can result in failure of a metal part.^{7–9} Besides weakening an appliance corrosion products can stain adjacent tooth surfaces.^{12–14} Corrosion can also release metallic ions into the oral cavity^{10–16} with adverse effects on the oral mucosa and the immunological system. The most common side effect is contact allergy.^{17–23}

The purpose of this study was to determine the surface morphological changes on stainless steel attachments and archwires, and NiTi archwires, following prolonged exposure to artificial saliva. The stainless steel wires were heat-treated to relieve stresses induced during manipulation and

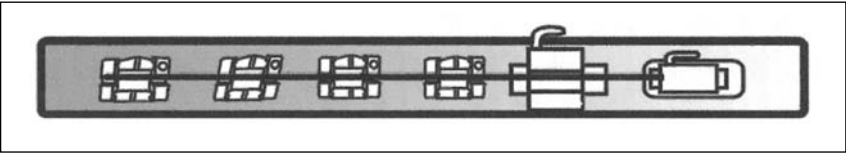


Figure 1. Diagram of a simulated fixed orthodontic appliance.

manufacture, and the brackets were welded to sectioned stainless steel bands.

Materials and methods

Simulated appliances were made from maxillary left first and second molar pre-formed bands sectioned and welded together to form straight bases 80 mm in length. Maxillary central incisor, canine, and first and second premolar brackets were attached to the base strip with a single weld, and first and second molar tubes were attached to the base strip with two welds each. The maxillary lateral incisor brackets were not welded to the base, but were ligated to the test “archwires”. All archwires were straight 60 mm lengths (Figure 1).

The stainless steel wires were heat-treated in an electric furnace (SMC Model, Kwangmyung Daicom, Korea) at 500 degrees Celsius for one minute then quenched in water. The composition of the alloy was then

analyzed using EDS (Energy Dispersive Spectroscopy, Superdry model, Kevex, USA). The stainless steel attachments were welded to the base with a RMO 660-2 welder (Rocky Mountain Orthodontics, USA).

The simulated appliances were immersed in artificial saliva with a pH 6.75 ± 0.15 (0.4 g NaCl, 0.4 g KCl, 0.80 g CaCl₂ • 2H₂O, 0.01 g Na₂S • 5H₂O, 1.0 g CO(NH₂)₂ (Urea), 1 L distilled water) in 50 mL polyethylene tubes, and maintained at 37 degrees Celsius in an incubator (Jeio Tech, IB-600 M Incubator, Korea).

Three hundred and twenty simulated appliances, divided into four groups according to the manufacturer and type of archwire, were tested (Table I). Each group included 80 samples subdivided into equal subgroups. The subgroups were immersed in artificial saliva and incubated for: 1 day (1D), 3 days (3D), 7 days (7D), 2 weeks (2W), 3 weeks

Table I. Materials used.

Materials	Types of alloy	Group	Manufacturer	Composition of alloy (weight per cent)						
				Si	S	Cr	Ni	Fe	Ti	Cu
Brackets 0.018 inch	SS		Tomy	2.38	3.84	20.36	9.42	64.01	–	–
Tubes 0.018 inch				1.41	2.24	19.46	8.92	67.97	–	–
Bands 0.13 x 4.6 mm				1.13	0.39	19.61	8.37	70.49	–	–
Archwires 0.016 x 0.022 inch	SS	A	Ormco	0.69	0.46	20.52	8.29	70.03	–	–
				1.60	1.95	18.71	8.21	69.54	–	–
	NiTi	C	Copper NiTi, Ormco	–	–	–	47.65	–	44.65	7.70
				–	–	–	53.38	–	44.25	2.30

SS: Stainless Steel

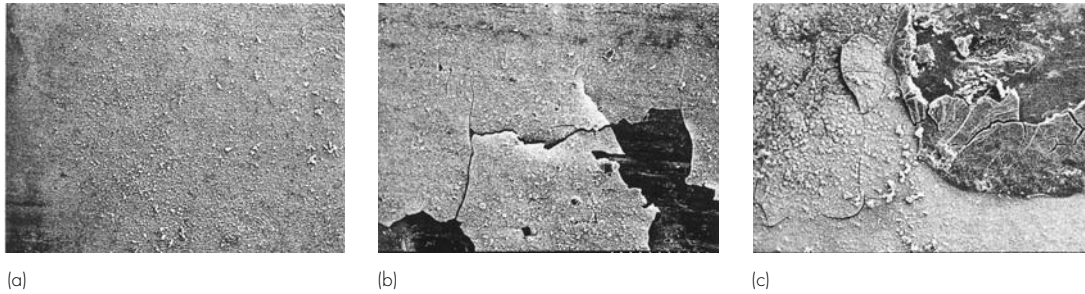


Figure 2. SEM photographs of selected archwires after immersion in artificial saliva for varying periods of time: (a) Group A, 1 day (b) Group A, 4 weeks (c) Group D, 8 weeks.

(3W), 4 weeks (4W), 8 weeks (8W) and 12 weeks (12W).

The colour change and surface morphology of each sample were observed macroscopically. The wire samples were then sectioned, and the surface morphology was examined using scanning electron microscopy (SEM, S-2700 model, Hitachi, Japan).

A spectrophotometer (CM-3500D spectrophotometer UV/visible, Minolta, Japan) was used to measure the surface reflectance of the wires at wavelengths ranging from 400–700 nm. The surface colour changes of the wires due to corrosion can be represented by their reflectance.

X-ray diffraction (XRD, D-Max Rint 240 model, Rigaku, Japan) was performed also to identify any oxides and hydroxides on the wire surface following immersion and incubation in artificial saliva. X-ray diffraction was carried out using Cu K α radiation. In the stainless steel archwires a 30–95 degree scan range was measured, and in the NiTi archwires a 30–150 degree scan range was measured. A scan rate of 4 degrees per minute was used for both archwires.

Results

The artificial saliva in the polyethylene tubes containing the stainless steel wires became cloudy with increasing immersion time, and rust coloured precipitates accumulated at the bottom of the tubes. After drying the simulated appliances, corrosion products could be seen on all stainless steel wires from the first day: it was particularly marked on the Group B samples. By day 7 the Group A and Group B wires were similar, and by 2 weeks

all stainless steel samples appeared to be covered in corrosion products. Those parts of the stainless steel wires opposite the bracket slots, particularly beneath the ligatures, were less brilliant than the wire between the brackets.

No evidence of corrosion of the NiTi wires (Groups C and D) was observed macroscopically until 12 weeks when there was a slight change in colour beneath the stainless steel ligatures. No other changes in surface appearance were observed.

Surface morphology

With increasing immersion time the oxide layer gradually thickened on the stainless steel wires. Small oxide deposits were visible on the Group A and Group B archwires from day 1 (Figure 2a). Over time the deposits increased slowly in size and number, and new oxides were deposited on previously formed layers (Figures 2b and 2c). By day 7 pit and crevice corrosion were observed on the Group A wires, and by week 12 corrosion products had formed around the ligated areas. These products “peeled off” when the ligatures were removed. Widespread surface corrosion, and cracks passing from the surface to the wire core were observed in the Group B wires.

Macroscopically, no corrosion was found on the NiTi archwires. However, some corrosion products were detected by the SEM as the immersion time increased. In Group C pits were visible from day 7 and by 2 weeks oxides had formed. By the third week the oxides had developed into oxide granules and thin particles, and by the fourth week crevice corrosion had developed into cracks. Similar

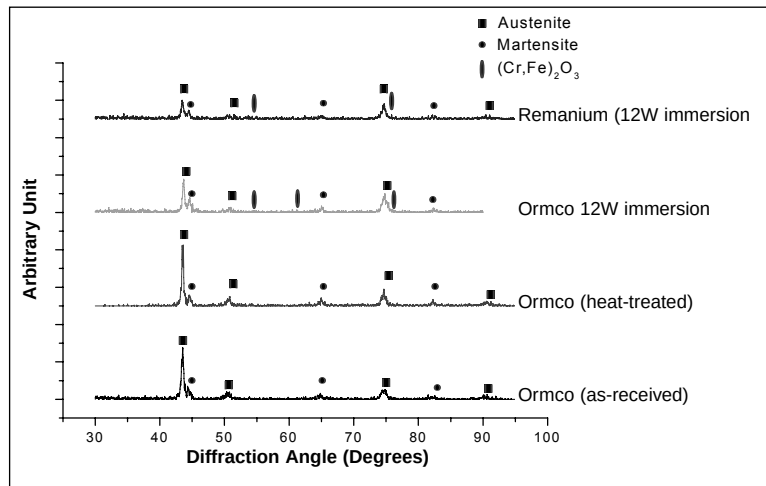
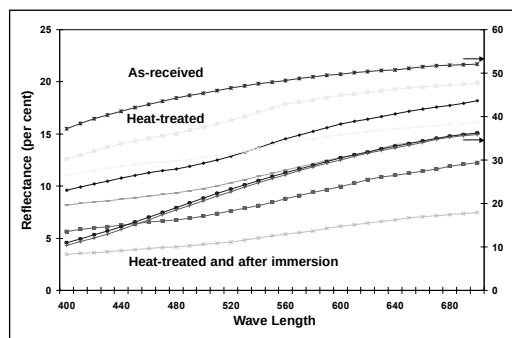
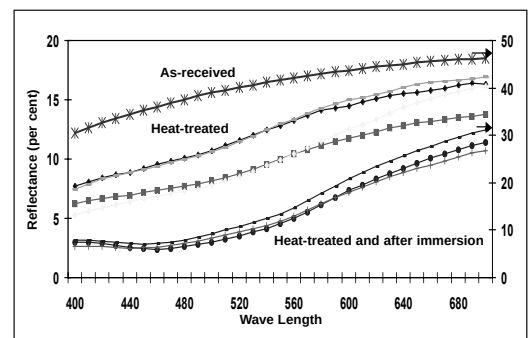


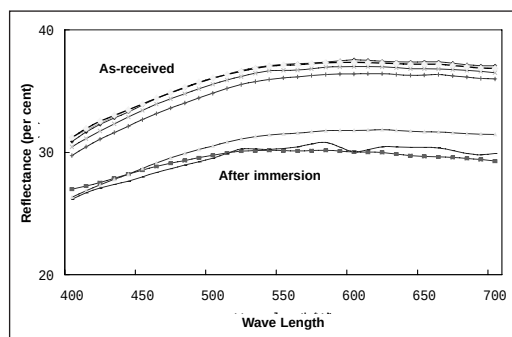
Figure 3. X-ray diffraction patterns of selected stainless steel archwires (Groups A and B).



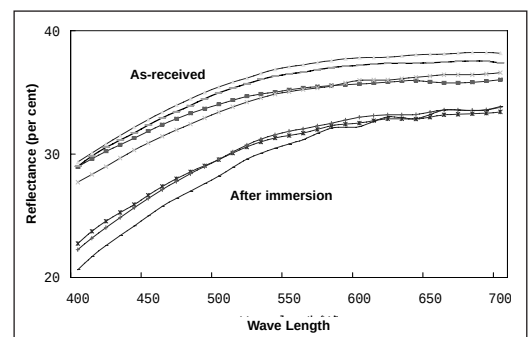
(a) Reflectance of Ormco Stainless Steel archwires (Group A).



(b) Reflectance of Remanium Stainless Steel archwires (Group B).



(c) Reflectance of Ormco NiTi archwires (Group C).



(d) Reflectance of Tomy Bioforce Sentalloy NiTi archwires (Group D).

Figure 4. Surface reflectance of selected archwires:

(a) Ormco stainless steel, (b) Remanium stainless steel, (c) Ormco copper NiTi, (d) Tomy Bioforce Sentalloy.

changes were observed in Group D. Disintegration of the wire surface beneath stainless steel ligatures was also observed.

Identification of surface oxides

In Groups A and B, the X-ray diffraction patterns of both the as-received and heat-treated wires were similar, but some differences were present after 12 weeks immersion in artificial saliva. In Group B, peaks corresponding to $\text{FeO}(\text{OH})$ and $\text{Fe}(\text{OH})_2$, in

addition to martensite, austenite, and $(\text{Cr,Fe})_2\text{O}_3$ formed by heat treatment, were observed (Figure 3).

In the NiTi archwires, NiTi, Ni_3Ti , and NiTi_2 phases were clearly seen both before and after immersion. There did not appear to be any other changes to the wires.

Spectrophotometry

In Group A, the reflectance of the as-received wire was 40–50 per cent, whereas that of the

heat-treated wire was 10–35 per cent (Figure 4). The immersed archwires gave a reflectance of less than 20 per cent, and there were no significant changes in reflectance with increasing immersion time. In Group B, the reflectance of the as-received wire was 30–40 per cent.

The reflectance of the as-received NiTi wires was 30–40 per cent, and of the immersed wires more than 20 per cent. Immersion time had no effect on the reflectance.

Discussion

In this study, the surface changes on simulated fixed orthodontic appliances and four different types of wire were determined. The stainless steel archwires were heat-treated prior to testing, and the brackets and buccal tubes were welded to uniform lengths of stainless steel band material. Welding can cause intergranular corrosion in stainless steel components such as bands, brackets and buccal tubes. It may also roughen and deform the surface increasing the possibility of corrosion.²⁴ In agreement with previous studies corrosion occurred around the welded orthodontic attachments.^{10, 25}

Heat treatment can lead to unstable oxide layers, greater surface roughness, and increased corrosion. In some cases small fragments of oxide may separate from the surface layer.²⁴ In the present study we observed corrosion not only on welded and heat-treated stainless steel components but also beneath stainless steel ligatures, and at the interfaces between the band material and brackets. The latter is crevice corrosion, and can lead to weld failure.

The colour changes were less marked on the NiTi wires, and occurred beneath the stainless steel ligatures. SEM observation of both NiTi wire groups showed pitting, accumulation of oxide products, and crevice and intergranular corrosion beneath the stainless steel ligatures with increasing immersion time.

Surface changes on the stainless steel and NiTi archwires were also detected by X-ray diffraction and spectrophotometry. In the heat-treated stainless steel wires, a $(\text{Cr,Fe})_2\text{O}_3$ phase α and γ phases were found. After 12 weeks of immersion, $\text{FeO}(\text{OH})$ and $\text{Fe}(\text{OH})_2$ phases were found also on the Group B wires.

However, peaks due to oxide and hydroxide products were not observed on the NiTi wires. The NiTi wires immersed in the artificial saliva and as-received had similar reflectance. There was a conspicuous decrease in reflectance when the stainless steel wires were heat-treated, and an even larger decrease in reflectance after immersion in artificial saliva (Figure 4).

Corrosion is usually observed in bracket slots and ligated areas, and tends to increase with time. Localised areas of corrosion on archwires have been postulated to weaken an archwire and, in some cases, cause it to fracture.²⁶ Movement of archwires in brackets may cause fretting corrosion which accelerates metal loss from both archwire and brackets. The corrosion resistance of the brackets, bands, tubes, and archwires relies to some extent on the presence of an undamaged passivated layer of chromium oxide on the metal surface. If these areas are damaged, reduced in area, or come in contact with aggressive ions, corrosion resistance is reduced.²⁷ Therefore, brackets that have been modified by grinding should be polished to limit corrosion caused by the release of Ni and Cr ions.

Corrosion of heat-treated stainless steel wires can be reduced by lowering the heat treatment temperature. Gjerdet and Hero²⁴ recommended that heat treatment should be carried out at the lowest temperature possible below 500 degrees Celsius. Furthermore, by heat-treating in an argon gas or vacuum environment the dense oxide or passivated layer is not damaged.

NiTi archwires have excellent corrosion resistance because the wire surface is covered with chemically stable passive layers similar to those found on titanium.²⁸ However, galvanic corrosion was observed between the NiTi archwires and the stainless steel brackets, bands, and ligature wires. Use of materials such as elastomeric ligatures instead of stainless steel ligatures will reduce the electromotive force responsible for corrosion, and will provide excellent corrosion resistance.

Conclusions

Uniform surface corrosion, which increased with time, was found on all heat-treated stainless steel archwires immersed and

incubated in artificial saliva for up to 12 weeks.

Crevice corrosion was observed under deposits of oxide, and at the interfaces between the brackets and band material. Such corrosion may weaken a wire or weld, leading to fracture. It is recommended that stainless steel archwires should be changed before crevice corrosion develops.

On the other hand, NiTi archwires exhibited only a slight colour change beneath stainless steel ligatures, and opposite contact areas with the stainless steel brackets and buccal tubes. NiTi archwires are significantly more stable and resistant to corrosion than stainless steel archwires.

Address for correspondence and reprints:

Professor Chung-Ju Hwang
Department of Orthodontics
College of Dentistry
Yonsei University
Seoul, Korea
Email: hwang@yumc.yonsei.ac.kr

References

- Jenkins GN. The physiology and biochemistry of the mouth. Cambridge: Blackwell, 1963: 284–303.
- Von Fraunhofer JA. Corrosion of orthodontic devices. *Semin Orthod* 1997; 3: 198–205.
- Maijer R, Smith DC. Biodegradation of the orthodontic bracket system. *Am J Orthod Dentofacial Orthop* 1986; 90: 195–8.
- Mueller HJ, Greener EH, Marker BC. Corrosion by external polarization of soldered orthodontic wires in cleanser solutions. *Am J Orthod* 1979; 76: 555–64.
- Johansson BI, Lemons JE, Hao SQ. Corrosion of dental copper, nickel, and gold alloys in artificial saliva and saline solutions. *Dent Mater* 1989; 5: 324–8.
- Berge M, Gjerdet NR, Erichsen ES. Corrosion of silver soldered orthodontic wires. *Acta Odontol Scand* 1982; 40: 75–9.
- Brown SA, Merritt K. Electrochemical corrosion in saline and serum. *J Biomed Mater Res* 1980; 14: 173–5.
- Brown SA, Merritt K. Fretting corrosion in saline and serum. *J Biomed Mater Res* 1981; 15: 479–88.
- Sarkar NK, Redmond W, Schwaninger B, Goldberg AJ. The chloride corrosion behaviour of four orthodontic wires. *J Oral Rehabil* 1983; 10: 121–8.
- Park HY, Shearer TR. In vitro release of nickel and chromium from simulated orthodontic appliances. *Am J Orthod* 1983; 84: 156–9.
- Barrett RD, Bishara SE, Quinn JK. Biodegradation of orthodontic appliances. Part I. Biodegradation of nickel and chromium in vitro. *Am J Orthod Dentofacial Orthop* 1993; 103: 8–14.
- Maijer R, Smith DC. Corrosion of orthodontic bracket bases. *Am J Orthod* 1982; 81: 43–8.
- Gjerdet NR, Erichsen ES, Remlo HE, Evjen G. Nickel and iron in saliva of patients with fixed orthodontic appliances. *Acta Odontol Scand* 1991; 49: 73–8.
- Kerosuo H, Moe G, Hensten-Pettersen A. Salivary nickel and chromium in subjects with different types of fixed orthodontic appliances. *Am J Orthod Dentofacial Orthop* 1997; 111: 595–8.
- Kerosuo H, Moe G, Kelsen E. In vitro release of nickel and chromium from different types of simulated orthodontic appliances. *Angle Orthod* 1995; 65: 111–16.
- Haudrechy P, Mantout B, Frappaz A, et al. Nickel release from stainless steels. *Contact Dermatitis* 1997; 37: 113–7.
- Bishara SE. Oral lesion caused by an orthodontic retainer: A case report. *Am J Orthod Dentofacial Orthop* 1995; 108: 115–7.
- Kalkwalf KL. Allergic gingival reaction to esthetic crowns. *Quintessence Int* 1984; 15: 741–5.
- Kerosuo H, Kullaa A, Kerosuo E, Kanerva L, Hensten-Pettersen A. Nickel allergy in adolescent in relation to orthodontic treatment and piercing of ears. *Am J Orthod Dentofacial Orthop* 1996; 109: 148–54.
- Bass JK, Fine HF, Cisneros GJ. Nickel hypersensitivity in the orthodontic patient. *Am J Orthod Dentofacial Orthop* 1993; 103: 280–5.
- Moffa JP. Biological effects of nickel-containing dental alloys. Council on dental materials, instruments, and equipment. *J Am Dent Assoc* 1982; 104: 501–5.
- Schrivver WR, Shereff RH, Domnitz JM, Swintak EF, Civjan S. Allergic response to stainless steel wire. *Oral Surg Oral Med Oral Pathol* 1976; 42: 578–81.
- Dunlap CL, Vincent SK, Barker BF. Allergic reaction to orthodontic wire: report of case. *J Am Dent Assoc* 1989; 118: 449–50.
- Gjerdet NR, Hero H. Metal release from heat-treated orthodontic archwires. *Acta Odontol Scand* 1987; 45: 409–14.
- Grimsdottir MR, Gjerdet NR, Hensten-Pettersen A. Composition and in vitro corrosion of orthodontic appliances. *Am J Orthod Dentofacial Orthop* 1992; 101: 525–32.
- Toms AP. The corrosion of orthodontic wire. *Eur J Orthod* 1988; 10: 89–97.
- Rhu JH, Kim SC. A study on the release of nickel and chromium from simulated orthodontic appliances. Master's thesis, Wonkwang University; 1998.
- Erdemir A, Carter WB and Hochman RE. A study of corrosion behavior of TiNi films. *Mater Science Engineering* 1985; 69: 89–93.