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Variations in surface characteristics and corrosion behaviour of metal brackets and wires in different electrolyte solutions

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SUMMARY The aim of this study was to assess the surface characteristics and to compare the corrosion potential of metal brackets and wires in environments containing different media. Four brands of metal brackets and two types of orthodontic wires [stainless steel and nickel–titanium (NiTi)] were investigated. An electrochemical assay was used to compare the corrosion potential (V) of the brackets and wires in different electrolyte media at 37°C. The test media were acidulated sodium fluoride (NaF) and pH 4 and pH 6 artificial saliva solutions. The data were analysed using analysis of variance with a predetermined significance level of $\alpha = 0.05$. Scanning electron microscopy (SEM) was used to observe surface defects and corrosion.

The results of the potentiodynamic curve showed that most brands of metal brackets were easily corroded in the NaF and pH 4 environments, while the NiTi and stainless steel wires were easily corroded in the pH 4 artificial saliva. SEM observations showed that defects or pitting corrosion occurred on the surfaces of the brackets and wires in all tested media.

Introduction

In the oral environment, orthodontic attachments are exposed to a number of potentially damaging physical and chemical agents, which might contribute to corrosion of the metal components of appliances (Maijer and Smith, 1986). Medical devices have generally been made with austenitic stainless steels designated by the American Iron and Steel Institute (AISI) as the '300 series'. Orthodontic bands, brackets, and wires are universally made of stainless steel containing approximately 8–12 per cent nickel and 17–22 per cent chromium (Grimsdottir *et al.*, 1992; Barrett *et al.*, 1993). Many investigations on the corrosion resistance of orthodontic metal appliances have been conducted (Rondelli and Vicentini *et al.*, 2000; Huang 2003; Shin *et al.*, 2003). A previous investigation demonstrated that metal ions are released from an orthodontic metal bracket at pH 4 (Huang *et al.*, 2004). A number of studies have also demonstrated that metal ions are released by all dental alloys *in vitro* and *in vivo* (Messer and Lucas,1996; Toumelin-Chemla *et al.*, 1996).

Dental cements and resins containing fluoride are used to prevent dental caries. Fluoride levels in the oral cavity vary according to the prophylactic treatment. Fluoride levels in toothpastes and mouth rinses can reach 1 per cent and, for eliminating enamel stains, can be close to 2 per cent; these substances have a pH range of between 3.5 and 7.0 (Toumelin-Chemla *et al.*,1996). Since the oral environment is particularly favourable for the biodegradation of metal due to its ionic, thermal, microbiologic, and enzymatic properties, it can be presumed that to a certain extent patients are exposed to the products of corrosion processes (Locci *et al.*, 2000).

The main clinical concern with the corrosion effects of metal brackets and wires is with regard to friction. Friction on orthodontic archwire–bracket combinations has been reported to be affected by factors such as the type of archwire and the bracket material (Loftus *et al.*, 1999), their size and shape (Ogata *et al.*, 1996), the width and slot dimensions (Peterson *et al.*, 1982), the surface composition, the roughness and cleanliness of the contacting surfaces (Kusy and Whitley, 1990), the bracket-to-archwire positioning in three-dimensional space (Kusy and Whitley, 1999), the ligature force (Keith and Jones,1993), the type of ligation (Riley *et al.*, 1979), and inter-bracket distances (Moore and Waters, 1993). With the straight wire technique, bracket–wire friction affects the sliding movement of the teeth during space closure or canine retraction. Corrosion defects on the surface of the orthodontic appliance will influence friction. There is less research concerning the surface characteristics of brackets and wires after corrosion in the oral environment.

The purpose of the present study was to assess the surface characteristics and to compare the corrosion potential of brackets and wires in different media simulating the oral environment.

Materials and methods

Four orthodontic wires, 0.016 inch (0.41 mm) nickel–titanium (NiTi; 3M, Unitek, Monrovia, California, USA), 0.016 × 0.022 inch (0.41 × 0.56 mm) NiTi, 0.014 inch (0.36 mm) stainless steel wire (SSW), and 0.016 × 0.022 inch

(0.41 × 0.56 mm) SSW, and four major orthodontic brackets, Unitek DynaLock twin-torque (3M, Unitek), Tomy metal base (Tomy Co., Tokyo, Japan), Ormco standard edgewise (Ormco Co., Orange, California, USA), and Ricketts (Dentarum Co., Ispringen, Germany), were tested in this study. The wires were cut into 50 mm long specimens. Each sample consisted of five pieces. All materials were cleaned by swabbing with acetone and placed in an ultrasonic container with distilled water for 10 minutes before testing.

The electrochemical corrosive breakdown of the metal brackets and wires was initiated using a method based on the description of Shih *et al.* (2000). Three electrolytes were used in the corrosive reaction. In group 1, artificial saliva containing 0.2 per cent acidulated phosphate fluoride [sodium fluoride (NaF); 0.2 per cent NaF + 0.17 per cent H_3PO_4, adjusted to pH 3.5 with lactic acid) was used as the electrochemical corrosive electrolyte and was maintained at 37°C. In the second and third groups, the electrochemical corrosive electrolytes were adjusted to pH 4 and pH 6 using lactic acid in artificial saliva. A cyclic potentiodynamic polarization machine CH Instrument 602C, Inc., Houston, Texas, USA, was applied from −800 mV in the anodic direction with a scan rate of 1 mV/s after dipping the specimen into the electrolyte for 1 hour. Each cyclic potentiodynamic polarization curve was printed out. The global polarization curves were assessed to determine the corrosion and breakdown potentials. A scanning electron microscope (SEM; ABT-150S, Topcon, Tokyo, Japan) was used to observe the surface morphologies of the metal brackets and wires. The data were analysed using analysis of variance with a predetermined significance level of α = 0.05.

Results

The cyclic potentiodynamic polarization curves for the metal brackets are shown in Figure 1a. The corrosion tendencies of different brands of brackets were statistically compared, and the corrosion potential [voltage, mean ± standard deviation (SD), Table 1] sequence from strong to weak was as follows: Ormco, NaF = pH 4 > pH 6; Unitek, (SD) NaF = > pH 6; Dentaurum, NaF = pH 4 > pH 6; and Tomy, pH 4 > NaF = pH 6.

The cyclic potentiodynamic polarization curves of the various waves are shown in Figure 1b. The corrosion tendencies of the different wires are indicated by the corrosion potential (voltage, mean ± SD, Table 2) sequence from strong to weak: 0.016 × 0.022 inch SSW, pH 4 = pH 6 > NaF; 0.014 inch SSW, pH 4 = pH 6 > NaF; 0.016 inch NiTi, pH 4 = pH 6 > NaF; and 0.016 × 0.022 inch NiTi, pH 4 = pH 6 > NaF.

SEM observations of the different brackets in the different media are shown in Figure 2a. The bracket surface of all brands in the normal artificial saliva group indicated that surface defects were related to bracket milling, pickling, or electropolishing procedures performed during the manufacturing process. In the pH 6 group, surface defects were similar to those of the normal artificial saliva group. In the pH 4 group, bracket surface defects and pitting corrosion were observed. In the NaF group, pitting corrosion and defects were similar to those of the pH 4 group.

For the different wires in the different media, the results of the SEM are shown in Figure 2b. They indicated that the wire surface defects were related to the wire drawing, pickling, or electropolishing procedures performed during the manufacturing process. The wire surface of the normal salivary group, for both the SSW and NiTi wire, exhibited scratches and pits on the surface (Figure 2b-A). The surfaces of the NiTi wires immersed in pH 4 and NaF media became rough and pitted due to corrosion (Figure 2b-C and 2b-D for the 0.016 × 0.022 inch and 0.016 inch NiTi groups, respectively). The surfaces of the SSW groups exhibited scratches and pitting corrosion with pH 4 and NaF treatment (Figure 2b).

Discussion

Maijer and Smith (1986) found that orthodontic brackets can exhibit different corrosion behaviour. The present results revealed similar findings. The surfaces of brackets and wires in different media exhibited various degrees of roughness. AISI-type 316L stainless steel alloy is currently used for bracket manufacturing (Matasa, 2000). Stainless steel owes its corrosion resistance to chromium, a highly reactive base metal. The alloy's corrosion resistance depends on a passive film, which spontaneously forms (passivation) and reforms (repassivation) in air and under most tissue fluid conditions (Sutow, 2001). Oxygen is necessary to form and maintain the film, whereas acidity and chloride ions can be particularly detrimental (Sutow, 2001).

From the potentiodynamic polarization curves, it is apparent that most brands of metal brackets showed higher corrosion tendencies in the pH 4 and NaF media (Figure 1a). It is known that corrosion of orthodontic alloys occurs in the intraoral environment regardless of the metallurgic structure of the alloy, and it is also known that the presence of manufacturing defects may accelerate the process (Sutow, 2001). SEM of the brackets showed existing surface defects in the normal artificial saliva group in the present study (Figure 1b). In an acidic condition, pitting corrosion was identified. As with Cl^- ions, fluoride ions (F^-) may penetrate into the metal/oxide film interface (Harzer *et al.*, 2001). The present results are in agreement with those findings; defects and pitting corrosion existed on the metal bracket surface in the NaF group (Figure 2a). As it is known that stainless steel will release nickel ions after corrosion occurs, a disadvantage with stainless steel bracket corrosion concerns patients with allergies to nickel and other specific substances. From the present results, it is recommended that substances with an acidic or fluoride content should be used with caution in

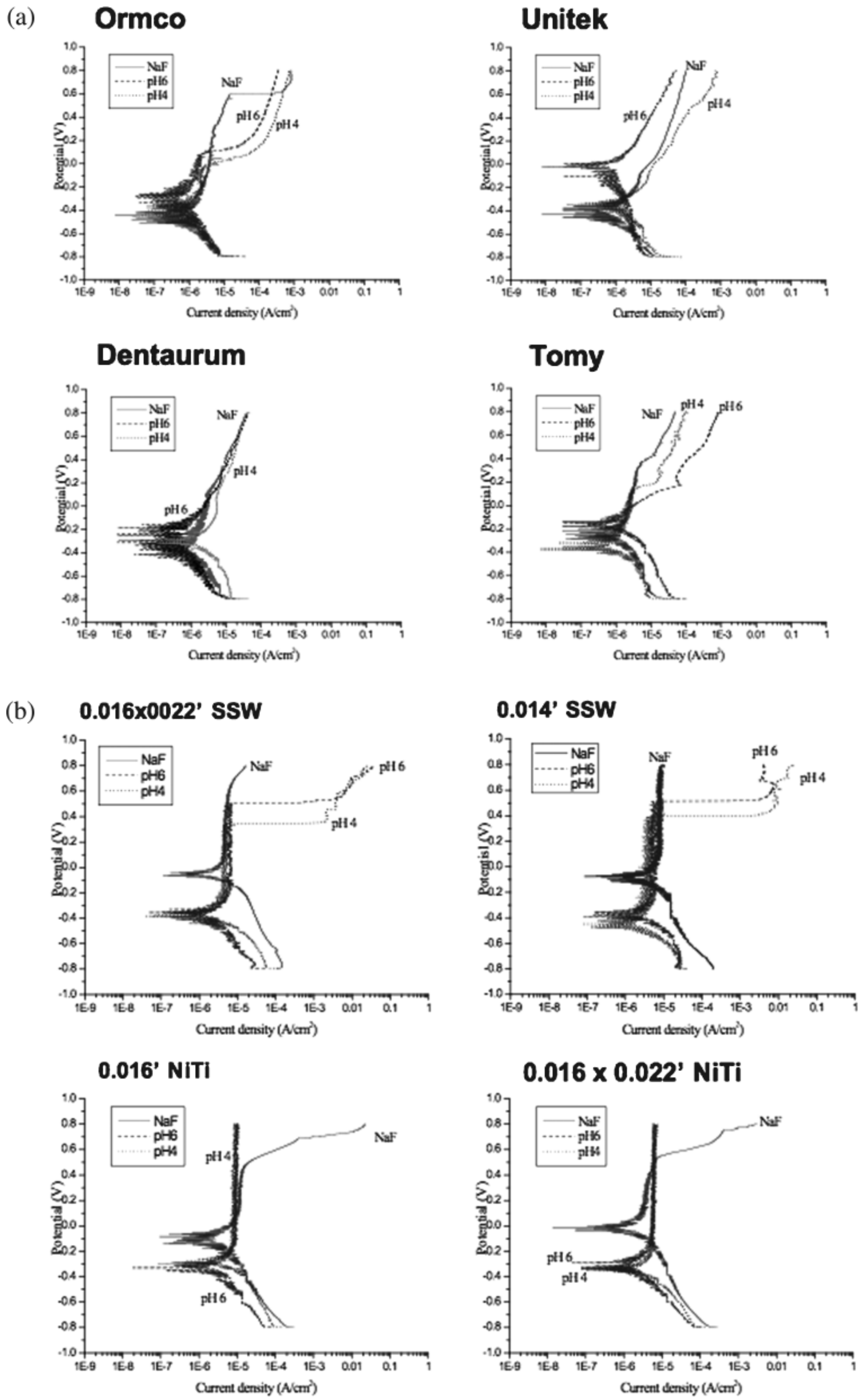

Figure 1 Electrochemical analysis. Cyclic potentiodynamic polarization curves of metal brackets (a) and stainless steel (SSW) and nickel titanium (NiTi) wire (b) in pH 4, pH 6, and NaF artificial saliva solutions.

Table 1 Results of electrochemical analysis of metal bracket (n = 5) cyclic potentiodynamic polarization potential (voltage, mean ± standard deviation).

	NaF	pH 4	pH 6	Analysis of variance
Ormco	−0.451 ± 0.087	−0.438 ± 0.093	−0.324 ± 0.118	F = 4.86, P = 0.016
Unitek	−0.412 ± 0.095	−0.417 ± 0.192	−0.082 ± 0.018	F = 11.96, P = 0.001
Dentaurum	−0.367 ± 0.069	−0.407 ± 0.081	−0.286 ± 0.052	F = 4.06, P = 0.045
Tomy	−0.271 ± 0.051	−0.346 ± 0.063	−0.256 ± 0.046	F = 4.02, P = 0.046

Table 2 Results of electrochemical analysis of orthodontic wires (n = 5) cyclic potentiodynamic polarization potential (voltage, mean ± standard deviation).

	NaF	pH 4	pH 6	Analysis of variance
0.016 × 0.022 inch stainless steel	−0.09 ± 0.013	−0.402 ± 0.101	−0.397 ± 0.189	F = 10.39, P = 0.002
0.014 inch stainless steel	−0.121 ± 0.009	−0.425 ± 0.105	−0.401 ± 0.101	F = 20.11, P = 0.000
0.016 inch nickel titanium	−0.126 ± 0.078	−0.358 ± 0.097	−0.345 ± 0.106	F = 9.54, P = 0.003
0.016 × 0.022 inch nickel titanium	−0.067 ± 0.019	−0.387 ± 0.095	−0.316 ± 0.102	F = 21.41, P = 0.000

Sample size is five in each test group.

patients undergoing orthodontic treatment. Titanium brackets were found to have reduced pitting and crevice corrosion (Harzer *et al.*, 2001). Replacing stainless steel brackets with titanium brackets could be considered.

Surface irregularities observed on the NiTi archwires may arise from the manufacturing process (Brantley, 2000). It was found in the normal salivary group that the NiTi wire surface showed irregularities or roughness in the SEM observations (Figure 2b). The present electrochemical studies indicated that pitting corrosion of NiTi wires occurred in a pH 4 solution. The mechanism might be from hydrogen penetrating the NiTi wire (Yokoyama *et al.*, 2003). Acid treatment causes the wire to become brittle, and under stress, the NiTi wire may fracture (Yokoyama, *et al.* 2003). Usually, titanium forms several oxides (during passivation, it forms TiO_2, TiO, and Ti_2O_5). The NiTi wire with the titanium oxide surface showed increased corrosion resistance. When Ti is exposed to water, TiO_2 is expected to form according to the reaction, $Ti + 2H_2O \rightarrow TiO_2 + 2H_2$. During this reaction, H+ ions are produced, increasing the pH. The resulting OH− anions are adsorbed onto the surface, where they create an electrical field for ion migration and subsequent oxide growth (Eliades and Athanasiou, 2002). This mechanism can explain the present results, as the surfaces of the NiTi wires in the pH 4 group showed defects (Figure 2b). Acid corrosion of NiTi wires increases the risk of wire fracture under the stresses of orthodontic treatment.

Fluoride ions can cause the breakdown of the protective passivation layer that normally exists on titanium and its alloys, leading to pitting corrosion (Schiff *et al.*, 2002). In the present study, the NaF corrosion potential was lower than pH 4 or pH 6 on the potentiodynamic curves (Figure 1b). This indicates that wires in the NaF medium still corroded, but the corrosion resistance was stronger than that of the NiTi wire in the pH 4 or pH 6 groups. However, SEM showed that the NiTi wire corrosion defects in the NaF group were more obvious than those in the pH 4 or pH 6 groups. That is probably because titanium easily dissolves in hydrofluoric acid that creates surface defects (Watanabe and Watanabe, 2003).

The present results showed that the surface of the SSW groups exhibited scratches and pitting corrosion under pH 4 and NaF treatment. This is similar to reports that 316 stainless steel in an acetic acid solution containing F^- ions showed pitting corrosion (Li *et al.*, 2001). The mechanism involves penetration of F^- ions into the metal/oxide film interface (Schiff *et al.*, 2002). In the present study, the surfaces of the brackets or wires showed roughness or defects before testing, and the corrosive potentials of stainless steel and NiTi were similar. Thus, after the specimens were treated in the corrosive media, the surface defects became more severe and obvious. These results are in agreement with other reports (Edie *et al.*, 1981; Kim and Johnson, 1981). One reason might be that 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 surface corrosion and pitting commence.

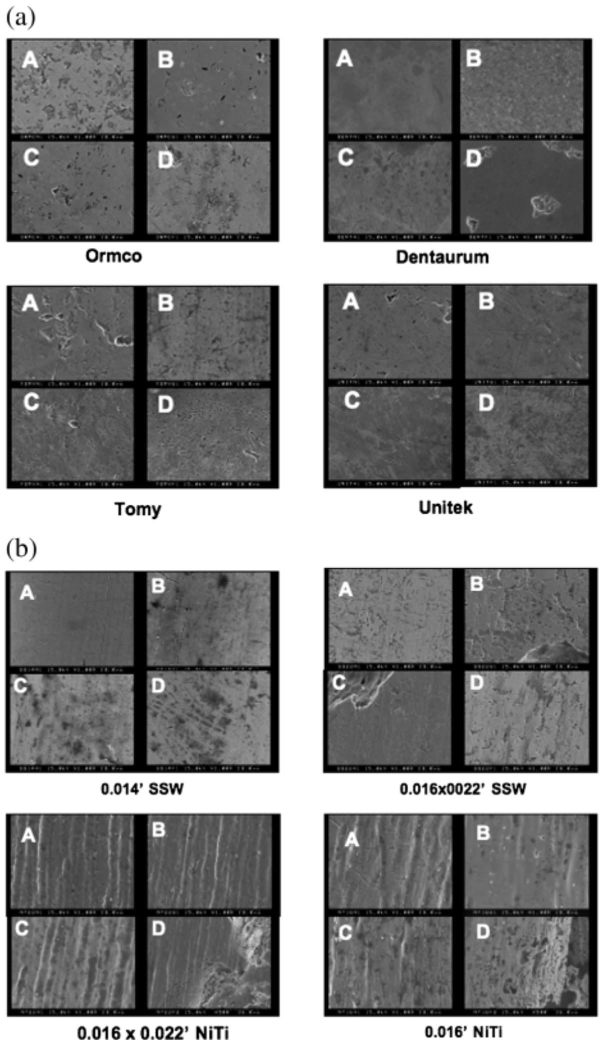

Figure 2 Scanning electron microscopy observations of different brands of bracket (a) and steel and nickel titanium wires (b) in different mediums. A, normal artificial saliva; B, pH 6 artificial saliva; C, pH 4 artificial saliva; D, NaF artificial saliva.

Conclusions

The corrosion resistances of metal brackets and wires in the present study were analysed by electrochemical methods. Most brands of metal bracket were easily corroded in the NaF and pH 4 environments. Potentiodynamic curves showed that NiTi wire and SSW were easily corroded in pH 4 artificial saliva. According to SEM, the bracket and wire surfaces showed defects or pitting corrosion in all tested media. The extent of surface roughness might influence friction. How the rough corroded surfaces of brackets and wires influence the orthodontic tooth sliding movement requires further investigation.

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