Corrosion-related Changes on Ti-based Orthodontic Brackets in Acetic NaF Solutions: Surface Morphology, Microhardness, and Element Release

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This study sought to investigate the effects of acetic NaF solutions on titanium and Ti alloy brackets. To this end, two different brackets were immersed in various NaF-containing solutions for three days. The Equilibrium Ti (EQ) bracket was composed of Ti only, whereas the Ortho 2 (OR) bracket was composed of Ti (base) and Ti-6Al-4V (wings). Brackets that were immersed in the acetic NaF solution of pH 3.5 yielded no reliable surface microhardness values due to corrosion. In other test solutions, however, there was minimal reduction (at best 3%) in microhardness. Further on microhardness, the values of the OR bracket at the base and wings were different. On the release of elements, it was significant only in the acetic NaF solution of pH 3.5. However, the release of Al (6.11 ± 0.93 ppm) and V (1.16 ± 0.40 ppm) in this solution was low. In conclusion, an acetic NaF solution of low pH could damage Ti-based orthodontic brackets.

Key words: Corrosion, Bracket, NaF solution

INTRODUCTION

Of late, titanium and Ti-6Al-4V brackets are introduced to overcome the deficiencies and disadvantages of stainless steel brackets[1]. Most notably in terms of health hazards, the Ni and Cr elements in stainless steel brackets are known to induce allergic, toxic, or carcinogenic effects[2-4].

An alpha Ti alloy is a commercially pure (CP) titanium alloyed with alpha-stabilizing elements such as oxygen and nitrogen. This alloy exhibits high creep strength and improved weldability. As for Ti-6Al-4V, it is an alpha-beta alloy. This alloy contains both alpha- and beta-stabilizing elements. Cr, Fe, Mn, Mo, and V are beta-stabilizing elements. The alpha-beta alloy shows high tensile strength and good creep resistance[5,6].

Titanium is known to possess excellent biocompatibility, corrosion resistance, and a lack of allergenicity as compared with many other metals. High corrosion resistance in Ti-based materials is mainly achieved by a thin oxide layer on the surface. When this oxide layer is damaged, the subsurface structure comes into contact with external body fluids. Since it takes a long time for the damaged surface to be repassivated, the release of elements during this period is inevitable[7,8]. One problem with the Ti-6Al-4V alloy is the potential development of toxicity by elements Al and V.

During orthodontic treatment, patients are frequently advised to use fluoride-containing products to prevent the risk of dental caries. Therefore, the use of fluoride-containing products such as toothpastes, dental gels, and rinses at a level of $100 - 10{,}000$ ppm has become a commonplace routine in daily life. Oral bacteria on dental plaque produces oral acids while they metabolize carbohydrates[9]. Subsequently, when released fluoride interacts with the oral acids, hydrofluoric acid (HF) is formed[10,11].

The purpose of the present study was to evaluate the effects of acetic NaF solutions on titanium and Ti-6Al-4V orthodontic brackets. To this end, changes in microhardness, surface morphology, and the release of elements from the brackets by HF were investigated.

MATERIALS AND METHODS

Brackets and test solutions
Two different Ti-based orthodontic brackets (a commercially pure (CP) titanium and a Ti alloy (Ti-6Al-4V)) were used in this study. Details of these brackets are presented in Table 1. In view of the experimental objective of this study, five different test solutions were prepared: distilled water (DW), two 0.1% acetic NaF solutions (pH 3.5 and 6), and two acetic acid solutions (pH 3.5 and 6). With the exception of distilled water, the pH values of the test solutions were adjusted using acetic acid.

Measurement of fluoride
The test solutions were prepared by mixing 0.1% NaF solution with acetic acid. To determine the change in fluoride concentration before and after the addition of acetic acid, fluoride concentrations in 0.1% NaF solution and acetic acid-added 0.1% NaF

Table 1 Brackets used in this study

Company	Brand/type	Position	Slot	Lot
Dentaurum Co. (Ispringen, Germany)	equilibrium® Ti (EQ) edgewise	Upper	0.022	345360
Ormco Co. (Glendora, USA)	Ortho 2 (OR) twin, G/O	1st Bicuspid	0.022	040681619

solutions were measured using a calibrated fluoride-specific electrode (96-09, Thermo Electron Corp., Beverly, USA). The latter was attached to an ion meter (model 720A+, Thermo Electron Corp., Beverly, USA) with an accuracy of 0.1 ppm. Before each measurement, the machine was calibrated from 20 to 50 ppm using a standard fluoride solution. Each measurement was repeated three times under the same conditions after diluting the test solution.

Elemental composition
Brackets (n=3) were embedded in an epoxy resin in a direction perpendicular to their longitudinal axis. Specimens were polished using SiC papers (#400, #1200), and then finely polished using alumina paste and a suspension. This was followed by ultrasonication in distilled water for five minutes and drying. The elemental compositions of the bracket base and wing components were evaluated more than three times by using an energy dispersive spectrometer (EMAX, Horiba, Kyoto, Japan) which was coupled to a scanning electron microscope (S4200, Hitachi Co., Tokyo, Japan). The accelerating voltage of the examination beam was 20 kV.

Measurement of microhardness
To measure microhardness, brackets were embedded in an epoxy resin and fully polymerized, and then polished as described above. Microhardness of the polished base and wing parts was evaluated using a Vickers hardness tester (MVK-H1, Akashi Co., Tokyo, Japan). To make microindentations (n=12 for each test condition), a 10-second dwell time and a 200-gf load were selected to facilitate measurement. After the first microhardness measurement, the specimens were immersed in 5 ml of each test solution for three days. After immersion, the specimens were cleaned with running water and the same microhardness test repeated using the same dwell time and load condition. Additional measurements were performed near the pre-measured position.

Measurement of released elements
The concentrations (ppm) of elements (Ti from EQ; Ti, Al, V from OR) released in the test solutions during immersion were analyzed using an inductively coupled plasma optical emission spectrometer (ICP-OES) (Optima 4300DV, Perkin-Elmer, Boston, USA). Brackets were immersed in the test solutions for three days. For each measurement, 1 ml of each test solution was diluted to become 10 ml. Five brackets were used for each test condition. In the present study, the lowest limit of a reliable measurement for Ti and V was 0.05 ppm, and that for Al was 0.02 ppm. However, taking into consideration the uncertainty of the measuring system and the specimens, a concentration less than these lowest limits was assumed to be 0.

Observation of surface morphology
Brackets (n=3 for each condition) were embedded in an epoxy resin, polished on the side surface as described above, and ultrasonicated in distilled water. At room temperature, the specimens were immersed in 5 ml of each designated test solution for three days. After which, the specimens were removed, cleaned, and dried. Surface morphology was observed using a scanning electron microscope (S-4200, Hitachi, Tokyo, Japan).

RESULTS

Measurement of fluoride
Table 2 shows the measured fluoride and estimated HF concentrations in the test solutions. As the pH value decreased from 6 to 3.5, the concentration of the fluoride ions decreased significantly from 434 ± 11 to 342 ± 15 ppm. HF concentration was determined by the difference between the fluoride concentration before (1st column in Table 2) and after (3rd column in Table 2) the addition of acetic acid to the 0.1% NaF solution.

Elemental composition
Figure 1 shows the elemental compositions of the base and wings of the tested brackets. The EQ bracket was composed of Ti only. For the OR bracket, the base was Ti and the wings Ti alloy (Ti-6Al-4V).

Measurement of microhardness
Table 3 shows the microhardness values of the tested brackets before and after immersion in the test

Table 2 Measured fluoride and estimated HF concentrations in solutions of pH 3.5 and 6

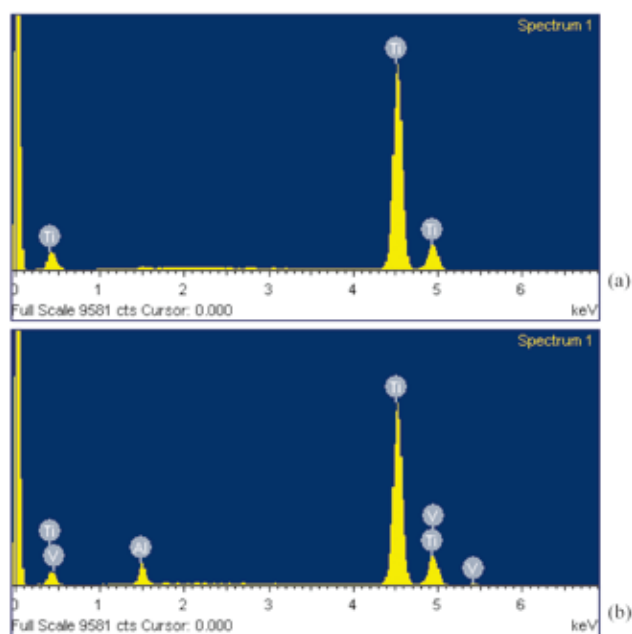| Solution	pH	F^- (ppm)	HF (ppm)
0.1% NaF	3.5	342 ± 15	103
(445 ± 12 ppm)	6	434 ± 11	11

Fig. 1 Elemental components of the tested brackets at the base and wings. (a) EQ base/wings and OR base; (b) OR wings

solutions. The EQ bracket showed similar microhardness values at both the base (182.3－186.6 Hv) and wings (183.4－186.2 Hv), before and after immersion in the test solutions. Conversely, the OR bracket showed different microhardness values for the different bracket components. The wings exhibited higher (340.5－342.1 Hv) values than the base (145.8－147.8 Hv). After immersion in acetic NaF solution of pH 3.5, the surfaces of the brackets were so severely damaged, such that it was not possible to accurately measure microhardness on the specimen surface.

In terms of comparison between test solutions, specimens immersed in NaF-containing solutions showed slightly lower microhardness values than those immersed in solutions which did not contain NaF.

Measurement of released elements
Table 4 shows the concentrations of the elements released from the brackets in the test solutions after immersion for three days. The EQ bracket released only Ti, whereas the OR bracket released Al, Ti, and V. The OR bracket released slightly more Ti (16.3±2.3 ppm) than the EQ bracket (9.1±1.5 ppm). Elemental release was significant only in acetic NaF solution of pH 3.5. In other test solutions, elemental release was negligible.

Observation of surface morphology
Figure 2 shows the surface morphologies of the brackets immersed in acetic NaF solution of pH 3.5 after three days. Be it the base or wings, both EQ

Table 3 Microhardness (Hv) values of the brackets before and after immersion in test solutions for 3 days

	EQ base		EQ wings	
	Before	After	Before	After
Dw	182.3 ± 7.3	180.5 ± 8.4	183.4 ± 8.3	181.6 ± 6.3
Acetic NaF_pH 3.5	186.6 ± 4.6		185.1 ± 5.7	
Acetic NaF_pH 6	184.2 ± 2.8	169.4 ± 4.4	184.5 ± 3.9	170.8 ± 5.4
Acetic_pH 3.5	185.6 ± 2.8	175.8 ± 6.9	186.2 ± 4.3	175.9 ± 4.8
Acetic_pH 6	185.3 ± 4.5	177.9 ± 6.7	184.7 ± 5.2	177.3 ± 6.3

	OR base		OR wings	
	Before	After	Before	After
Dw	147.8 ± 5.7	145.3 ± 7.2	342.1 ± 5.5	340.2 ± 7.1
Acetic NaF_pH 3.5	146.3 ± 4.6		340.7 ± 6.4	
Acetic NaF_pH 6	147.2 ± 3.8	142.7 ± 5.1	342.1 ± 16.9	331.6 ± 9.5
Acetic_pH 3.5	145.8 ± 4.2	143.1 ± 6.4	340.5 ± 15.7	334.3 ± 15.9
Acetic_pH 6	146.6 ± 3.4	144.4 ± 6.8	340.6 ± 10.1	336.5 ± 12.9

Dw: distilled water; Acetic NaF_pH 3.5: acetic NaF solution of pH 3.5; Acetic NaF_pH 6: acetic NaF solution of pH 6; Acetic_pH 3.5: acetic acid solution of pH 3.5; Acetic_pH 6: acetic acid solution of pH 6

Table 4   Concentrations of the elements released from the brackets in different test solutions

	EQ		OR	
	Ti	Al	Ti	V
Dw	0	0.1±0.0	0	0.1±0.0
Acetic NaF_pH 3.5	9.1 ± 1.5	6.1±0.9	16.3±2.3	1.2±0.4
Acetic NaF_pH 6	0	0.1±0.0	0	0.1±0.0
Acetic_pH 3.5	0	0.1±0.0	0	0.1±0.0
Acetic_pH 6	0	0.1±0.0	0	0

Ti and V: less than 0.1 ppm was assumed to be 0; Al: less than 0.1 ppm was assumed to be 0.
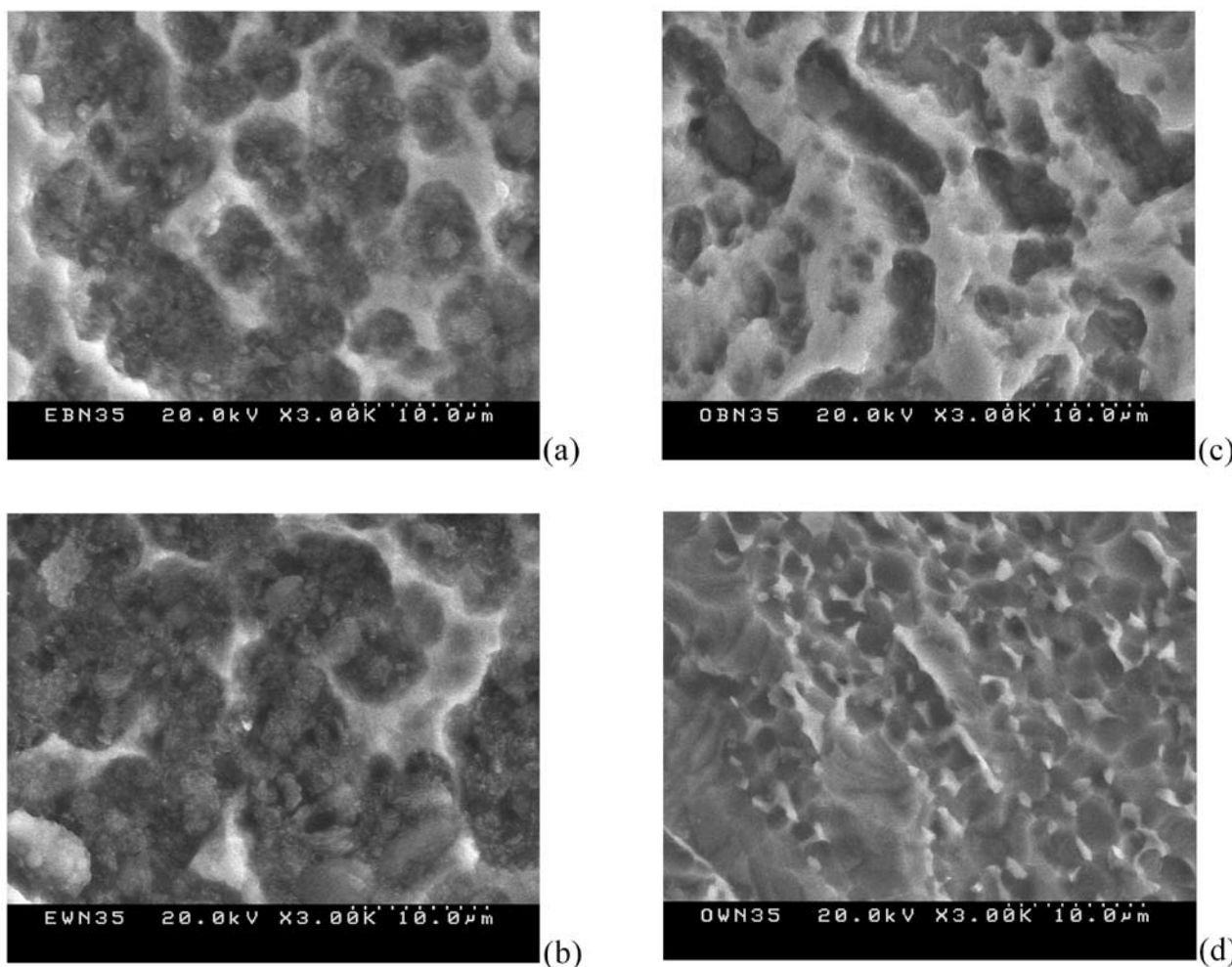

Fig. 2   Surface morphologies of the brackets after being immersed in acetic NaF solution of pH 3.5 for three days. (a) EQ bracket base; (b) EQ bracket wing; (c) OR bracket base; (d) OR bracket wing.

and OR brackets exhibited an extremely corroded surface morphology. As seen in Fig. 2, an irregular remaining pattern was left on the surface. However, in other test solutions, no visible surface modification was observed.

DISCUSSION

Ti can exist in more than one crystallographic form. At room temperature, Ti has a hexagonal close-packed crystal structure (hcp) and it is called the alpha phase (alloy). This alpha phase can be selectively stabilized at room temperature by alloying

Ti with other elements such as aluminum (Al), niobium (Nb), molybdenum (Mo), and vanadium (V). The Ti-6Al-4V alloy contains Al and V as stabilizers, and it is classified as an alpha-beta alloy[5,6]. The brackets used in the present study had two different element compositions: Ti and Ti alloy (Ti-6Al-4V). Titanium is biocompatible with human tissues and it is resistant to corrosion. When titanium is exposed to air, a thin and stable oxide layer spontaneously forms on the surface. This thin layer consists of amorphous or low-crystalline and non-stoichiometric TiO_2. The layer on Ti-6Al-4V is almost the same as that of titanium, but it contains a small amount of aluminum (Al) oxide[12,13].

Ideally, a 0.1% NaF solution should contain 452.4 ppm of F^- ion and 547.6 ppm of Na^+ ion. To adjust the pH of the solution, acetic acid was used instead of the commonly used phosphoric acid. Moreover, since acetic acid is produced by oral bacteria as a result of fermentable carbohydrate metabolism, using acetic acid seemed to be a more logical and natural choice than phosphoric acid. In a test solution of pH 6, the HF concentration was 11 ppm. In a phosphoric acid-adjusted solution, however, the solution with a pH of 4.5 had formed 12 ppm of HF[14]. This difference was due to the acidity of the used acid solution. Since phosphoric acid is stronger than acetic acid, less acid is needed to lower the pH value. When NaF interacts with acetic acid or phosphoric acid, HF is formed. Subsequently, HF can react with TiO_2, thus dissolving the protective oxide layer by forming TiF_3, TiF_4, or $TiOF_2$ on the surface[10,11].

After immersion in an acetic NaF solution of pH 3.5, the two brackets showed different surface morphologies. A similar remaining pattern on the base and wings of the EQ bracket implied that the constituent element of both bracket components could be identical. However, the OR bracket showed different remaining patterns on the base and wings. The top layer of the wings was completely removed. On the other hand, much of the top layer was left on the base. As shown in the EDS analysis, these differences could arise from differences in the elemental composition of the same bracket. The entire surface of the EQ bracket and the base of the OR bracket showed different remaining patterns although they were composed of the same element, Ti. These differences might be attributed to the manufacturing process or surface treatment[15]. The EQ bracket was produced by machined-out, forged, and rolled profiles. As for the OR bracket, it consisted of two completely different parts and these parts were joined together by laser welding.

The Vickers hardness test showed identical values of the EQ bracket at the base and wings. This was because the constituent element of EQ bracket was only Ti. The brackets immersed in acetic NaF solutions showed slightly lower microhardness values than those immersed in acetic acid solutions and distilled water. The difference should be due to the HF formed in the solutions. The other reason might be related to hydrogen embrittlement. Abundant hydrogen ions in the test solution of a lower pH can be absorbed into metals or alloys through interatomic diffusion. The absorbed hydrogen ions may react with oxides or carbides, leading to the degradation of mechanical properties and fracture of the material. Such degradation was observed in the titanium and titanium alloy which were immersed in a saline or fluoride solution[16,17]. In the acetic NaF solution of pH 3.5, reliable measurements were not possible because the surface sustained extensive damage due to a high quantity (103 ppm) of HF. Unlike the EQ bracket, the OR bracket showed very different microhardness values at the base and wings. These differences stemmed from the differences in constituent elements between the base and the wings. Nonetheless, after immersion in the test solutions, both the base and wings of OR bracket showed a similar decreasing pattern in microhardness as observed in the EQ bracket.

Through the damaged oxide layer, HF dissolution of the constituent elements occurred. The brackets immersed in an acetic NaF solution of pH 3.5 released element(s) while being immersed in the solution for three days. Ti was the only element released from the EQ bracket. Conversely, the OR bracket released Al (6.11 ± 0.93 ppm), Ti (16.32 ± 2.33 ppm), and V (1.16 ± 0.40 ppm). This result implied that the elements were preferentially released. Regarding their composition by weight (approximately 90 wt% Ti, 6 wt% Al, 4 wt% V), more Al might be released or that less Ti and V might be released.

In the oral cavity, the released elements are a potential source of toxicity. Titanium is biocompatible with human tissues. As a possible essential trace element, V can inhibit cellular proliferation and can be cytotoxic against macrophages and fibroblasts[18,19]. V can accumulate in the liver, kidneys, bone and spleen, but is expected to be excreted through urination[20]. The estimated daily intake of the US population ranges from 10 to 60 μg[21]. However, exposure to heavy V dust can induce asthma and rhinitis. Nonetheless, in general, the toxicity of V compounds is low[22]. Furthermore, since the orthodontic use of brackets has a limited service life, the level of V release (for three days in a solution with high level of HF) as demonstrated in this study may not cause serious damage.

CONCLUSIONS

According to the results of this study, the HF formed in acetic NaF solutions induced corrosion on the surface of Ti-based orthodontic brackets. In a low concentration (11 ppm), the effect of HF was similar to that of distilled water. In a high concentration (103 ppm), the level of corrosion by HF was severe. It was necessary to include the latter test condition in this study because in the oral cavity, a high concentration of fluoride with a long reaction time with acetic acid will occur owing to the routine use of fluoride-containing products for caries prevention.

In the acetic NaF solution of pH 3.5, the brackets were so severely corroded such that it was not possible for any reliable or reproducible surface microhardness measurements. In other test solutions, however, only minimal reduction in micro-hardness was observed. With the OR bracket, two different microhardness values were obtained for different component parts: 145.8－147.8 Hv for the base and 340.5－342.1 Hv for the wings. On the release of elements, it was significant only in the acetic NaF solution of pH 3.5. However, the release amounts of Al (6.11 ± 0.93 ppm) and V (1.16 ± 0.40 ppm) were low. In other test solutions, elemental release was negligible.

Based on the results of this study, the use of Ti-based orthodontic brackets did not seem to be safe if they are used with products that contain a high concentration of fluoride for an extended period of time under acidic conditions.

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