Original Article

Sensitivity of Titanium Brackets to the Corrosive Influence of Fluoride-Containing Toothpaste and Tea

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Abstract: Titanium brackets are used in orthodontic patients with an allergy to nickel and other specific substances. In recent studies, the corrosive properties of fluoride-containing toothpastes with different pH values were investigated. The present in vivo study tested how the surfaces of titanium brackets react to the corrosive influence of acidic fluoride-containing toothpaste during orthodontic treatment. Molar bands were placed on 18 orthodontic patients. In these same patients, titanium brackets were bonded on the left quadrants and stainless steel brackets on the right quadrants of the upper and lower arches. Fifteen patients used Gel Kam containing soluble tin fluoride (pH 3.2), whereas 3 used fluoride-free toothpaste. The brackets were removed for evaluation by light microscopy and scanning microscopy 5.5 to 7.0 months and 7.5 to 17 months after bonding. The quality and quantity of elements present were measured by scanning microscopy. Macroscopic evaluation showed the matte gray color of titanium brackets dominating over the silver gleam of the steel brackets. The plaque accumulation on titanium brackets is high because of the very rough surface. Pitting and crevices were observed in only 3 of the 165 brackets tested. The present in vivo investigation confirms the results of in vitro studies, but the changes are so minor that titanium brackets can safely be used for up to 18 months. Wing surfaces should be improved by modifying the manufacturing process. (*Angle Orthod* 2001;71:318–323.)

Key Words: Titanium brackets; Corrosion by fluorides; Acidic toothpaste

INTRODUCTION

The use of titanium brackets is advantageous in the orthodontic treatment of patients with an allergy to nickel and other specific substances.[1] However, the results of recent studies investigating the corrosive properties of fluoride-containing toothpastes differed with respect to the pH value of the environment.[2–7,9,10] Boere[2] used a polarization resistance technique (an electrochemical corrosion test procedure in vitro) and observed a large decrease in polarization resistance with increasing fluoride concentration at pH 4. Toumelin-Chemla et al[11] tested the corrosive properties of fluoride-containing toothpastes on titanium in vitro and found substantial corrosion processes in the fluoridated acidic media. Reclaru and Meyer[9] suggested that fluoride ions are the only ions acting on the protective layer of titanium and causing localized pitting and crevice corrosion. He found weak galvanic currents within a pH range of 6.2 to 3.5 in tests involving artificial saliva. However, in confined areas where fluoride ions were present, titanium and other dental alloys underwent a corrosive process in the form of crevices and pitting when the pH dropped below 3.5. Kusy et al[5] found in depth profile of titanium, oxygen, carbon, and nitrogen that the bulk structure was $>$95%, but in the near surface region some 200 to 300 Å in depth, the titanium metal was present with ever-increasing quantities of carbon, oxygen, and nitrogen. Therefore, the surface of brackets is not a titanium-rich alloy. Homula et al[4] suggested that the smooth, Teflonlike surface of titanium, because of a thin layer of titanium oxide, prevents direct contact between the metallic atoms on the surface of the wire and the bracket, thus reducing interatomic adhesion and friction. The existing data were obtained from in vitro experiments and are not directly applicable to the conditions in the oral environment.

The present research tested the corrosive influence of acidic fluoride-containing toothpaste on titanium brackets in vivo during orthodontic treatment by comparing titanium and steel material.

MATERIALS AND METHODS

Eighteen orthodontic patients, 8 children (mean age 12.5 years) and 10 adults (mean age 22.3 years), were selected

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TABLE 1. Distribution of Patients, Kind of Toothpaste, and Orthodontic Wires

		Group F+ Acidic Fluoride Toothpaste (Gel Kam)			Group F− Fluoride-free Toothpaste (Putzi)		
	Patients, n	Twistflex Wire	Nitinol Wire		Twistflex Wire	Nitinol Wire	
Children	8	4	3	7	0	1	1
Adults	10	4	4	8	2	0	2
Total	18	8	7	15	2	1	3

TABLE 2. Number of Investigated Brackets and Wires

	Brackets					
	Children		Adults		Total	
Variable	Titanium	Steel	Titanium	Steel	Titanium	Steel
Group F+[a]	67	39	69	32	136	71
Twistflex wire	31	16	38	7	69	23
Nitinol wire	36	23	31	25	67	48
Group F−[b]	12	9	17	10	29	19
Twistflex wire	0	0	17	10	17	10
Nitinol wire	12	9	0	0	12	9
Total	79	48	86	42	165	90

[a] F+ indicates fluoride in toothpaste.
[b] F− indicates no fluoride in toothpaste.

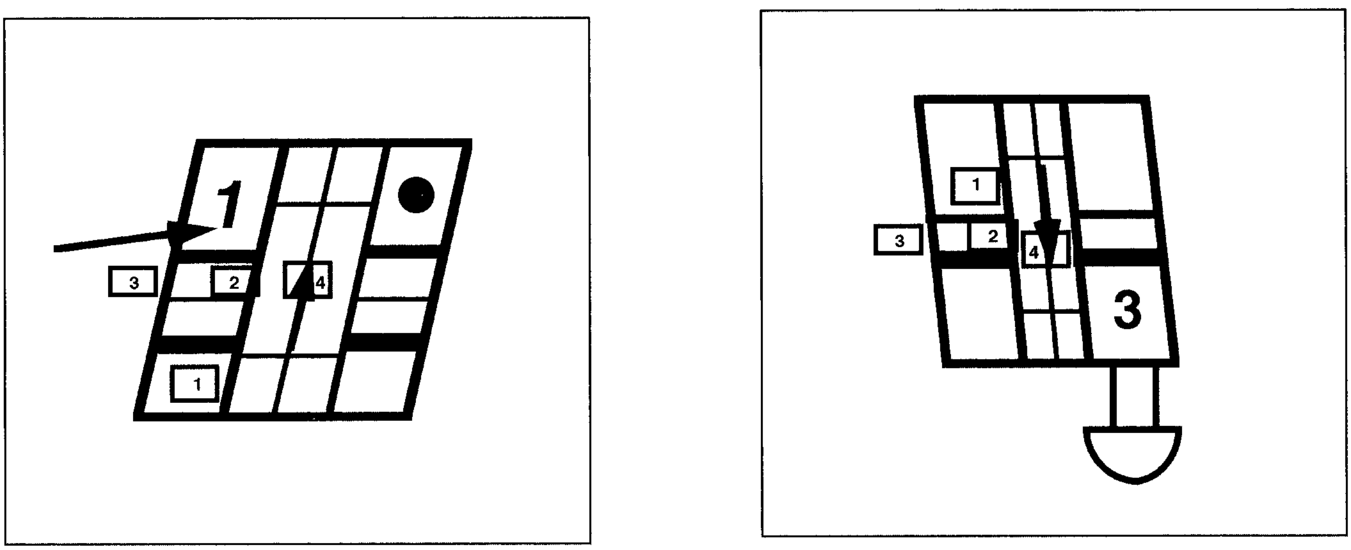
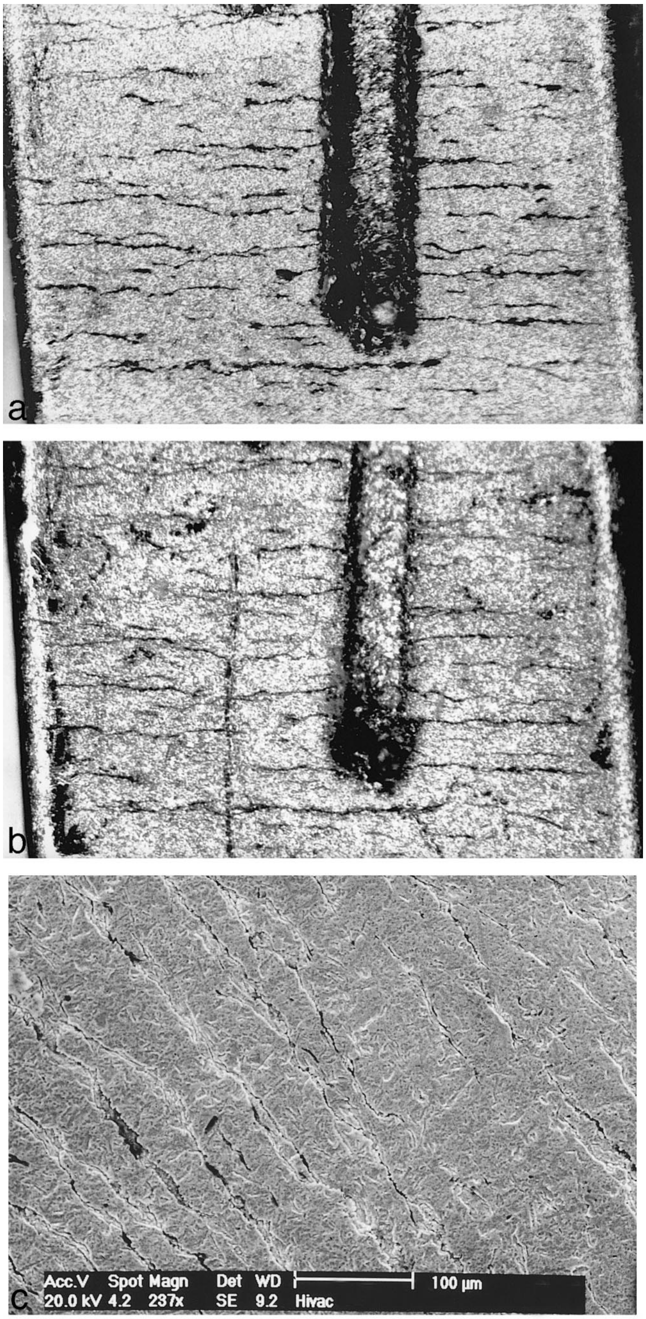


FIGURE 1. Measurement points at the brackets: 1 = bracket wing, 2/4 = bracket slot, 3 = at the side of bracket (→ detail region of Figures 2a and 2b).

for the investigation (Table 1). All patients received a fixed orthodontic appliance with bands at the molars and brackets at the incisors, canines, and premolars. Titanium brackets (Dentaurum, Pforzheim, Germany; German material no. 3.7065, titanium grade 1) were used on the left side in the upper and lower jaws, whereas steel brackets were used on the right side. Two manufacturing steps are used for the production of titanium brackets. In the first step, a profile is cold rolled and in the second step the slots are milled.

All patients were right handed, resulting in more intensive brushing on the left jaw side. This side was chosen because the mechanical stress and cleaning effect of brushing the left side is higher in right-handed patients. For daily brushing (every morning and evening), 15 patients (7 chil-



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Element	Wt %	At %	K-Ratio	Z	A	F
F K	1.01	2.51	0.0010	1.0984	0.0932	1.0001
TiK	98.99	97.49	0.9888	0.9988	1.0001	1.0000
Total	100.00	100.00				

Element	Net Inte.	Bkgd Inte.	Inte.Error	P/B
F K	0.66	0.63	17.21	1.05
TiK	462.03	3.25	0.47	142.16

FIGURE 2. (a) One of the 5 in vitro tested brackets which had been rinsed for 170 minutes with Gel Kam solution. Bracket is shown before rinsing (region at wing, see arrow, Figure 1). (b) Bracket from Figure 2a after rinsing. No change and no sign of corrosion are present. (c) Element analysis in 1 titanium bracket, which was rinsed for 14 days in green tea solution.

dren and 8 adults) used Gel Kam toothpaste (Colgate, Hamburg, Germany) containing soluble stannous fluoride (pH 3.2; group F+). Three patients (1 child and 2 adults) served as controls and brushed with a fluoride-free Putzi toothpaste (Dental Kosmetik, Dresden, Germany). This product contains a pH ranging from 9.1 to 9.7 (group F−). The choice of a fluoride-free dentifrice is normally less often practiced for daily tooth brushing, but for the methodological design to exclude any fluoride influence, the use of fluoride-free dentifrice was necessary. All patients used same type of toothbrushes (Oral B, Frankfurt/Main, Germany). Nickel-titanium and steel twistflex wires were used for orthodontic treatment. These wires were fixed to the brackets with elastomeric ligatures. However, because of mastication and occlusion, the wires moved with resulting friction and attrition. This attrition is strongest in steel twistflex wires. Groups were additionally subdivided into those with nickel titanium wires and those with steel twistflex wires (Table 2). The patients kept a written record of food intake and tooth brushing. They were asked to note other potential fluoride intake, eg, tea. Black and green teas contain additional fluoride and complicated the investigations. However, many orthodontic patients drink tea, and for this reason, this influence was taken into account. The oral hygiene status was recorded every 2 months by using the Oral Hygiene Index[8] with plaque staining (Mira 2-tone solution).

In a period of 5.5 to 7.0 months after bracket fixation, 2 titanium and 1 steel bracket were removed from each patient and tested for corrosion pitting and crevices. These brackets were replaced with new ones. All titanium brackets were removed after a treatment period ranging from 7.5 to 17 months. Five titanium brackets were tested in a Gel Kam solution for a duration of 170 minutes for comparison with in vitro conditions. Every 10 minutes, the brackets were rinsed in an ultrasonic bath with 80% alcohol. Additional 12 titanium brackets and 12 steel brackets were tested in green and black tea solutions (6:6 of each bracket and tea kind). The brackets were put in a green and black tea solution with a temperature of 50°C to 55°C for 14 days. For analysis of corrosion processes, 4 predetermined measurement points were recorded from the brackets before and after treatment (Figure 1). Brackets that became detached during treatment were excluded from the evaluation. The investigation involved 165 titanium brackets and 90 steel brackets randomized from each group and contact time in the mouth (Tables 2 and 3). An MZ 12 stereo microscope (Leica, Frankfurt, Germany) and a DSM 982 Gemini scanning microscope (Carl Zeiss, Jena, Germany) were used for microscopic analysis. The quality and quantity of elements, in particular, fluoride, tin and titanium, were registered on 17 titanium and 7 steel brackets by scanning microscopy.

Statistical evaluation was performed with the SPSS program.[12] The results are given as arithmetic means ± standard deviation. For statistical analysis, the χ^2 test was applied ($P < .05$) for 18 orthodontic patients. For microscopic

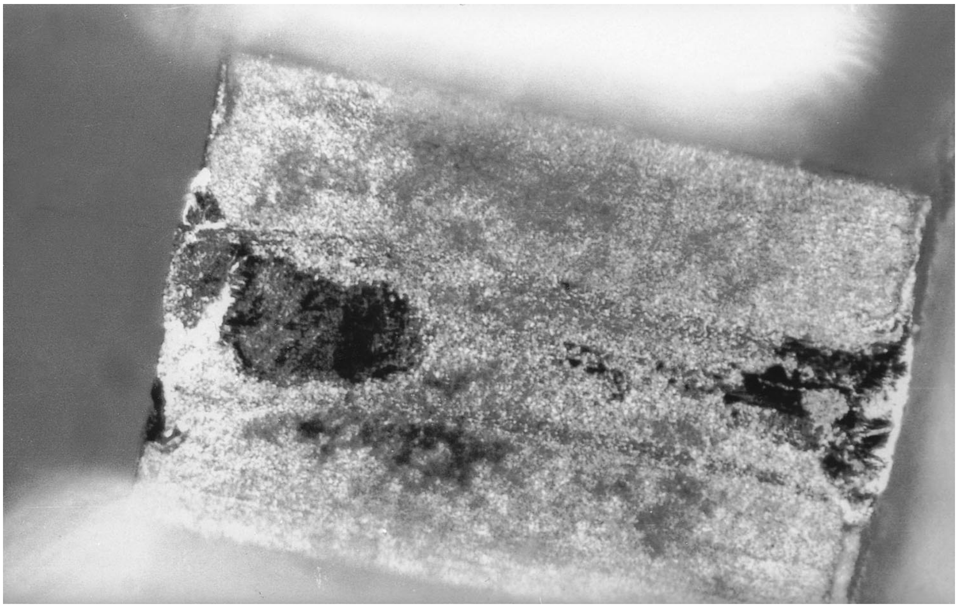


FIGURE 3. Traces of mechanical stress at the bottom of slot, point 2 between the wings (see Figure 1) of titanium bracket caused by the friction of twistflex wire.

TABLE 3. Duration of Bonded Brackets in the Mouth (Time of Fluoride Contact)[a]

Time, mo	Titanium Bracket Group F+	Titanium Bracket Group F−	Total	Steel Bracket Group F+	Steel Bracket Group F−	Total
2.5–5.0	35	8	43	18	2	20
5.5–7.0	44	7	51	13	4	17
7.5–17.0	57	14	71	40	13	53
Total	136	29	165	71	19	90

[a] F+ indicates fluoride in toothpaste; F−, no fluoride in toothpaste.

TABLE 4. Plaque Accumulation (Brown) in Patients With Tea Consumption (Green and Black)

Group F+[a]	Children Tea +, n = 5	Children Tea−, n = 3	Total Tea+	Adults Tea+, n = 4	Adults Tea−, n = 6	Total
Titanium bracket	20	1	21	23	20	43
Steel bracket	9	0	9	5	16	21

[a] F+ indicates fluoride in toothpaste.

TABLE 5. Change of Color and Plaque on Titanium Brackets (n = 165)

Measuring Point/ Discoloration	Group F+[a] n	Group F+[a] %	Group F−[b] n	Group F−[b] %
1	9	5.4	0	0
2	77	46.7	18	11
3	1	0.6	0	0
Plaque (brown)	64	38.8	2	1.2*

[a] F+ indicates fluoride in toothpaste.
[b] F− indicates no fluoride in toothpaste.
* $P \leq .05$.

evaluation, 165 titanium brackets and 90 steel brackets were investigated. Elements were analyzed in 33 of 165 titanium brackets and 19 of 90 steel brackets.

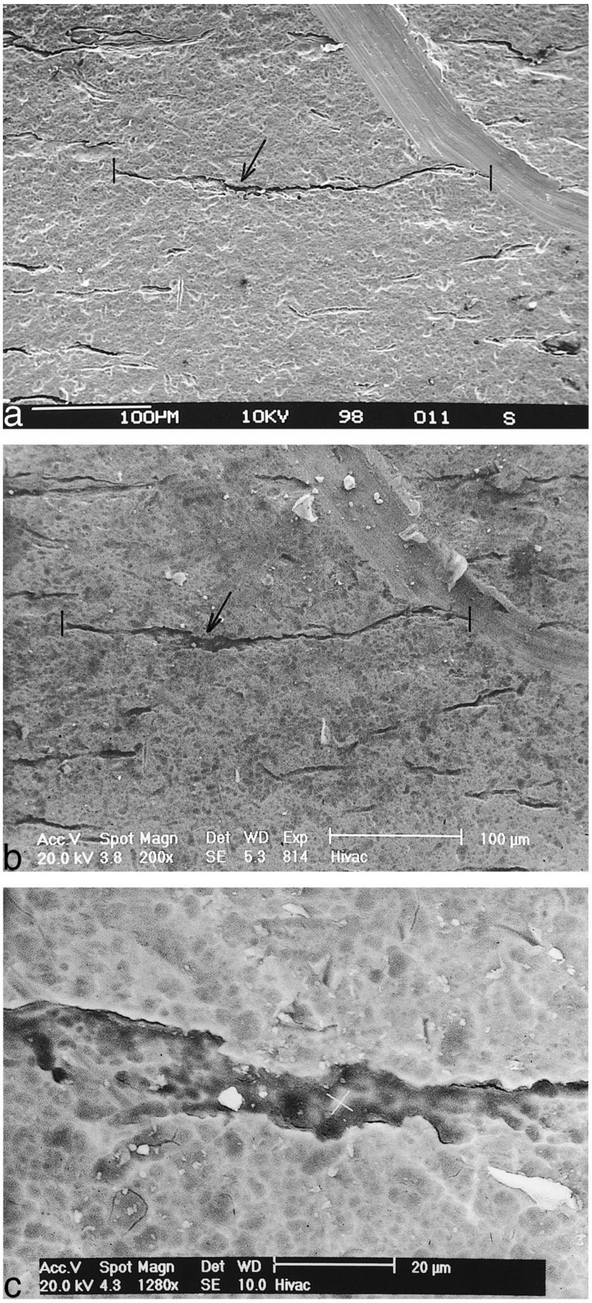
RESULTS

The Oral Hygiene Index ranged from 1.0 to 2.0 in all patients. Nine patients representing the F+ group stated that they drank black or green tea (Table 4). In vitro testing of the 5 brackets, which had been rinsed for 170 minutes with Gel Kam solution, showed no change and no sign of corrosion (Figure 2a,b). In vitro testing of the 24 brackets, which had been rinsed for 14 days with green and black tea solution, showed a very small amount of fluoride (1.01 wt%) with a high integrated error (17.21; Figure 2c).

Macroscopic evaluation showed the matte gray color of the titanium brackets dominating over the silver gleam of the steel brackets. Eight weeks after bonding, the titanium brackets had darkened in color. Regardless of the toothpaste used, the plaque accumulation on the titanium brackets was greater than in steel brackets. In 11 of 15 patients using Gel Kam, the teeth and brackets had yellow-brown coatings caused by the acidic stannous fluoride in the toothpaste and encouraged by the rough surface of the titanium (Tables 4 and 5).

Microscopic evaluation of 165 titanium and 90 steel brackets revealed traces of mechanical action caused by the friction of the wires and ligatures at the bottom of the slot between the wings of the brackets, but there was no significant difference among the brackets, wires, and toothpastes used (Figure 3; Tables 4 and 5).

Microscopic signs of the corrosion process are pits, crevices, and their extensions, but as the surface of the titanium



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Detector Type: UTW, Sapphire Resolution: 126.40 Lsec: 100

Element	Wt %	At %	K-Ratio	Z	A	F
C K	30.11	56.15	0.1108	1.0988	0.3346	1.0005
O K	11.15	15.61	0.0116	1.0803	0.0962	1.0001
F K	0.00	0.00	0.0000	1.0152	0.1210	1.0002
CoL	1.05	0.40	0.0024	0.9093	0.2509	1.0001
NaK	1.08	1.06	0.0031	1.0108	0.2867	1.0005
P K	0.58	0.42	0.0047	1.0003	0.7964	1.0090
ClK	0.99	0.62	0.0092	0.9790	0.9243	1.0289
TiK	55.04	25.74	0.5127	0.9198	1.0120	1.0008
Total	100.00	100.00				

Element	Net Inte.	Bkgd Inte.	Inte. Error	P/B
C K	25.78	0.39	1.98	66.10
O K	7.08	1.29	4.09	5.49
F K	0.00	1.38	0.00	0.00
CoL	0.52	1.62	28.13	0.32
NaK	3.70	2.78	6.88	1.33
P K	5.10	10.03	7.63	0.51
ClK	9.15	11.37	4.95	0.80
TiK	318.56	6.74	0.57	47.26

bracket is very rough because of the manufacturing process (cold rolling), the corrosion process can be identified only from an extension of existing pitting. In clinical testing, fissures, present at the wings of 3 titanium brackets in 2 patients (Gel Kam), seemed to be extended after 1 and 7 months, respectively. Scanning microscopy revealed that the length of a crevice was almost the same after the use of fluoride toothpaste (325.5 and 315.3 μm, respectively), but the width was doubled (10.6μm to 24.5μm; Figure 4a,b). In a special analysis of elements in the crevice, no fluoride occurred (Figure 4c).

Analysis of the elements in 17 titanium and 7 steel brackets revealed a very infrequent occurrence of fluoride at the 0,1% level, which was detected in only 2 titanium and 2 steel brackets of 3 patients. In 1 titanium bracket, from a patient in the group F− with tea consumption, analysis revealed a small amount of fluoride similar to the in vitro test.

DISCUSSION

The surface structure and the color of titanium and steel brackets are very different. The surface of the rolled wings of titanium brackets is very rough, and the biocompatibility of titanium supports plaque adherence. These are the reasons for significantly more plaque accumulation and a more marked change of color with titanium brackets. The slots of titanium brackets are not as rough as the wings because the slots are milled and not rolled. Deeper and wider crevices were found in the wings of only 3 of the 165 titanium brackets investigated (2%). This was possibly caused by the slight deformation associated with the removal process of the bracket and also confirms the in vitro results of Boere,[2] Toumelin-Chemla et al,[10] and Reclaru and Meyer.[9] These latter authors reported the occurrence of a corrosion potential in a fluoridated acidic media with a pH below 4.0 or 3.5. The pH of Gel Kam is 3.2, but the findings with deeper and wider crevices at the wings of 3 of 165 brackets are insignificant. The reasons for the differences between the in vitro and the in vivo experiments might be the short exposure time of the fluoride ions in the toothpaste to the titanium of the brackets, as well as to the heterogeneity of the outer layers where the titanium metal was present with increasing amounts of oxygen, nitrogen, and carbon.

The patients were instructed to brush their teeth for 3 minutes twice a day. However, the results confirm those of

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FIGURE 4. (a) Scanning microscopy picture from wing of 1 titanium bracket (region 1, Figure 1) before bonding at the tooth. (b) Scanning microscopy picture from wing of the same titanium bracket from Figure 4a after bonding and use of fluoride toothpaste for 7 months. The length of crevice was almost the same (I—I), but the width was doubled (:→:). Compare Figures 4a and 4b before and after treatment. (c) Analysis of elements shows no occurrence of fluoride in the crevice (spot measurement; penetration depth 5 to 7 μm).

Reclaru and Meyer[9] with respect to the crevice potential. The presence of fluoride ions does not affect the crevice potential of different alloys, including titanium, when the pH values are between 6.15 and 3.5. On the other hand, at pH 3, the crevice potential of titanium becomes negative at −55 mV vs SCE (Saturated Colomel Electrode). Thus, titanium undergoes a corrosion process in the form of crevices and pitting from pH 3.5 onward. In conclusion, the aggressiveness of the environment at pH 3 is such that it is no longer possible to maintain passivation zones, and titanium will, therefore, undergo a continuous degradation. The low rate of brackets with crevices is caused by the rinsing effect of saliva, water, and food that dilutes the fluoride ion concentration. Analysis of the elements in these brackets with deeper crevices revealed no fluoride. Fluoride was found only in tea-consuming patients, but the in vitro experiments showed this to be a very small amount with a high variation.

An adverse effect of the application of titanium brackets is their rough and smooth surface with high plaque accumulation. This upper layer is very biocompatible and serves as a depot for bacteria and electrolytic medium for different ions. The manufacturer should modify the production process and mill the entire bracket, but this is only of minor influence of the plaque adherence. Nevertheless, the comparison of Figures 4a and 4b shows that the surface of the bracket after 7 months is less prone to gather debris and plaque. The reason may be tooth brushing and attrition by hard food.

CONCLUSIONS

1. Titanium brackets show higher plaque accumulation and more discoloration than steel brackets. This is caused by the rough surface with a smooth outer layer. Biocompatibility should be improved by modifying the manufacturing process, but this influence is less than in steel brackets.
2. In contrast to the results of in vitro investigations, pits and crevices are found under acidic conditions below pH 3.5 in only a few brackets. The reason for this difference might be the short reaction time of fluoride ions and dilution by saliva and liquids.
3. The combined use of titanium brackets in combination with the use of acidic fluoride dentifrice and fluoridated foods is completely harmless for the bracket and does not give rise to corrosion.

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