Corrosion and permanent fracture resistance of coated and conventional orthodontic wires

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The corrosion processes are presumed to have negative consequences on biocompatibility, aesthetic appearance and the frictional behavior between the bracket and the guiding arch during orthodontic treatment. A group of new guiding arches are the coated orthodontic wires. The present *in-vitro* study investigated the corrosion behavior and permanent fracture resistance of eight coated wires of different dimensions. Five superelastic nickel titanium (NiTi) wires (Titanol® Low Force River Finish Gold and Gold 2: Forestadent Corp.; Titanol® Superelastic tooth colored: Forestadent Corp.; Bioforce Sentalloy Ionguard™: GAC Corp.; NiTi Imagination™: GAC Corp.), two β-titanium-wires (TMA Low Friction Ionguard: Ormco Corp.; TMA Low Friction Ionguard Purple: Ormco Corp.) and one steel wire (Stainless Steel Imagination™: GAC Corp.) were selected. For comparison reasons three uncoated arch wires (Rematitan® Lite Dimple: Dentaurum Corp.; Titanol® Low Force River Finish: Forestadent Corp.; Bioforce Sentalloy™: GAC Corp.) were included in the investigation. Surface modifications were made of teflon, polyethylene and by ion implantation. The corrosion processes have been carried out by the use of a specialized electrochemical cell. In a second experimental series the wires were exposed to mechanical stresses. Finally, all wires were examined in a scanning electron microscope. The results indicated that teflon coating prevented the corrosion of the wires. As expected, the β-titanium wires did not corrode either. The other wires showed rupture potentials between 187 mV and 602 mV (NHE). After mechanical stress testing the wires could be subdivided into three groups. In the first group no differences could be recognized, the second group showed changes in their crystallographic structure and in the last group the teflon coating was peeled off from the surface of the wires.

1. Introduction

The corrosion behavior of orthodontic wires has often been a topic in publications. Especially the number of dissolved ions in the electroyte was investigated. It was shown that the nickel content in the alloy is not proportional to the number of nickel ions in the solution during the corrosion process [6, 11]. Several authors evaluated the corrosion behavior of NiTi and stainless steel wires as being equal. Kappert *et al.* found that alloys on steel or nickel basis show pitting and area corrosion. Their rupture potentials were below 600 mV. Titanium alloys showed better corrosive properties [9]. Growing numbers of orthodontic treatments and the increasing prevalence of nickel allergy in the population ask for a minimization of the nickel loss from orthodontic wires in the oral cavity. This especially holds for NiTi wires. Even wires of the same alloy but from different manufacturers show a variety of characteristics with regard to structure, homogeneity and surface roughness [1, 9, 15].

A group of studies dealt with the comparison of *in vitro* and *in vivo* investigations. Holland described a connection between corrosive results and the composition of the electrolyte [8]. He recommended the use of *Fusayama* artificial saliva [4] because of its comparable results to clinical tests. Clinically tested wires showed less corrosive defects than wires in *in vitro* tests [10]. The first destruction by corrosive effects on clinically used wires could not be seen before six months.

A possible nickel sensitivity being induced in a patient by NiTi wire could not be clarified thus far. Some authors found no effect on the patients [12] and others described a desensitization of the patients by the use of nickel containing materials [13]. Several authors recommend the use of nickel free devices for the treatment of patients, who are already sensitized to nickel, as cases of allergic reactions to nickel containing orthodontic devices have already been reported [2, 7, 11]. Manufacturers try to comply with these requests by the development of coated wires or differing surface treatments of conventional orthodontic wires. It was the aim of this study to compare the corrosion behavior and the permanent fracture resistance of wires with different

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surface modifications with the behavior of standard orthodontic wires.

2. Materials and methods

2.1. Materials

This study focused on five orthodontic nickel titanium wires, two beta-titanium wires and one stainless steel wire, with surface modifications made of teflon, polyethylene or ion implantation. For comparison reasons, three uncoated wires were included in the study. Table I lists information on wire type, the surface modifications, alloy compositions and the manufacturers of all investigated wires. Only minor variations can be observed in the chemical composition of the NiTi wires, although their mechanical behavior differs significantly. The arches were tested in the dimensions 0.46 mm × 0.64 mm, 0.41 mm × 0.56 mm and 0.41 mm × 0.41 mm. This is a representative sample of the current situation of today's market.

2.2. Experimental procedure

The corrosion behavior of the wires was tested by exposure to anodic polarization in a modified Fusayama saliva to speed up corrosion processes. A first characterization of the wires was made by recording current densities versus polarization potentials to obtain rupture potentials. A reaction between the wire and the electrolyte can be observed when the polarization value is higher than the rupture potential of the specimen. Afterwards, all wires were polarized for 10 min with a voltage higher than the rupture potentials to generate corrosion. Subsequently the wires were examined with a scanning electron microscope (SEM, Philips XL20, The Netherlands), to document surface alterations due to corrosion.

A specialized electrochemical cell (Fig. 1) was used with a Ag/AgCI reference electrode (Type B 2820, Schott, Germany), a platinum counter electrode, a Haber-Luggin capillary (salt bridge), a gas inlet/outlet for N_2 rinsing and a combined heating and temperature controlling system to regulate the temperature of the electrolyte according to body temperature. The electrochemical cell was driven by a potentiostate (electronics workshop, Department of Chemical Physics, University of Bonn) and a function generator (TG 230, Thurlby-Thandar, England). Additionally, a vertically moveable inert glass rod was integrated for mechanical load application. The set-up was computer controlled and data were taken over by a personal computer via an A/D converter board [15].

A defined length of 30 mm of each of the specimens was exposed as electrode to the electrolyte. Modified Fusayama artificial saliva [7] at 37 °C was chosen as electrolyte as the results of corrosion experiments tend to correlate best with the results obtained from natural saliva. The composition of the saliva used is listed in Table II.

2.3. Cyclic mechanical loading test

In a second experimental series ten wires of each type were exposed to mechanical stresses to simulate the intra oral situation during mastication. Five thousand bending cycles were carried out with a glass rod that moved vertically over a distance of 1.5 mm with a frequency of 1 Hz. The wires were fixed with a free wire length of 20 mm by macor rods with specialized wire clamps (Fig. 2) in distilled water. Twenty millimeters correspond to a typical free bending length comparable to the space between two teeth around an extraction site. Bending experiments were conducted at an ambient temperature of 37 °C.

TABLE I Orthodontic wires used in this study. Chemical composition given either by the manufacturer or determined by EDX analysis

Manufacturer	Product	Dimension (mm^2)	Alloy type, chemical composition	Surface/coating	Short name
Dentaurum	Rematitan Lite Dimple	0.46 × 0.64	Nickel-titanium, 53.2% Ni, 46.8% Ti	Uncoated	DRLD
Forestadent	Titanol River Finish	0.46 × 0.64 0.41 × 0.56 0.41 × 0.41	Nickel-titanium, 53.0% Ni, 47.0% Ti	Uncoated, polished	FTRF
Forestadent	Titanol River Finish Gold	0.46 × 0.64 0.41 × 0.56 0.41 × 0.41	Nickel-titanium, 53.0% Ni, 47.0% Ti	Polyethylene	FTG
Forestadent	Titanol River Finish Gold 2	0.46 × 0.64 0.41 × 0.56 0.41 × 0.41	Nickel-titanium, 53.0% Ni, 47.0% Ti	Polyethylene	FTG 2
Forestadent	Titanol Superelastic Zahnfarben	0.46 × 0.61	Nickel-titanium, 53.0% Ni, 47.0% Ti	Teflon	FTSZ
GAC	Bioforce Sentalloy	0.46 × 0.64	Nickel-titanium, 52.4% Ni, 47.6% Ti	Uncoated	GBS
GAC	Bioforce Sentalloy longuard	0.46 × 0.64	Nickel-titanium, 52.4% Ni, 47.6% Ti	Ion implanted	GBSI
GAC	NiTi Imagination	0.46 × 0.61	Nickel-titanium, 52.4% Ni, 47.6% Ti	Teflon	GNTI
GAC	Stainless steel Imagination	0.46 × 0.61	Stainless steel, 72.0% Fe, 18.0% Cr, 8% Ni	Teflon	GSSI
Ormco	TMA low friction longuard	0.41 × 0.56	Titanium-molybdenum, 78% Ti, 11% Mo, 6% Zr, 4.5% Sn	Ion implanted	TMAI
Ormco	TMA low friction longuard (purple)	0.41 × 0.56	Titanium-molybdenum, 78% Ti, 11% Mo, 6% Zr, 4.5% Sn	Ion implanted	TMAP

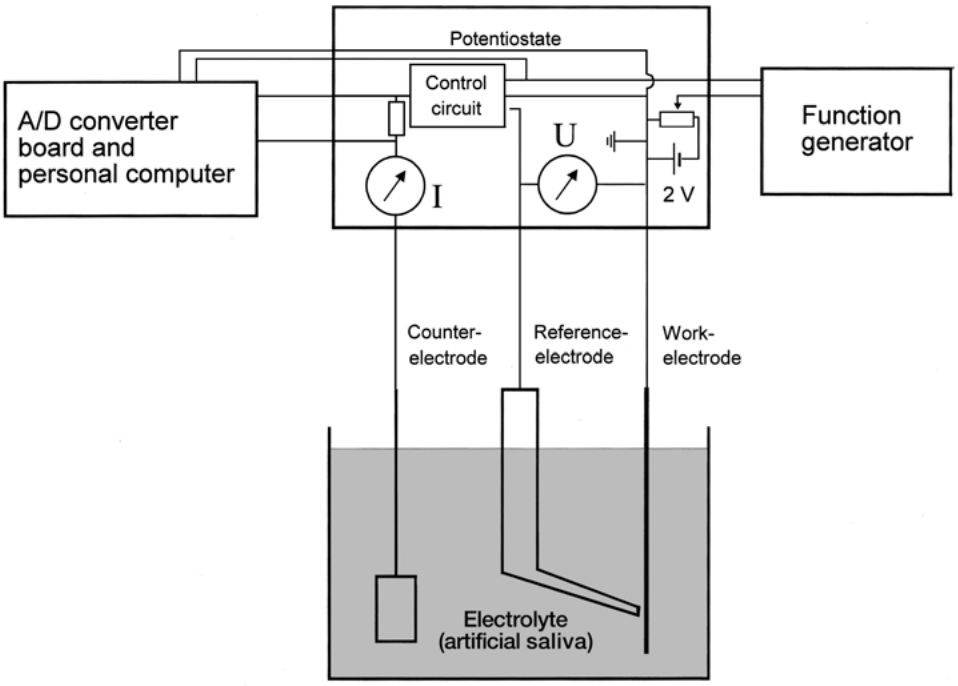

Figure 1 Schematic experimental set-up of the electrochemical cell.

2.4. Scanning electron microscopy (SEM)

To make surface changes visible a sample of each wire was examined with the SEM. The as-received state was compared with tested wires. The surfaces were cleaned with ethanol and a 5–10 mm piece was fixed to a specimen holder. The polyethylene- and teflon-coated wires had to be sputtered to improve the picture quality in the SEM. The SEM XL 20 was computer controlled and the scanned surfaces were saved to hard disk.

TABLE II Composition of the modified artificial Fusayama saliva used in this study

Components	($mg\ l^{-1}$)
Sodium chloride	400
Potassium chloride	400
Calcium chloride-dihydrate	795
Sodium hydrogen phosphate-1-hydrate	690
Potassium rhodanide	300
Sodium sulfide	5
Urea	1000

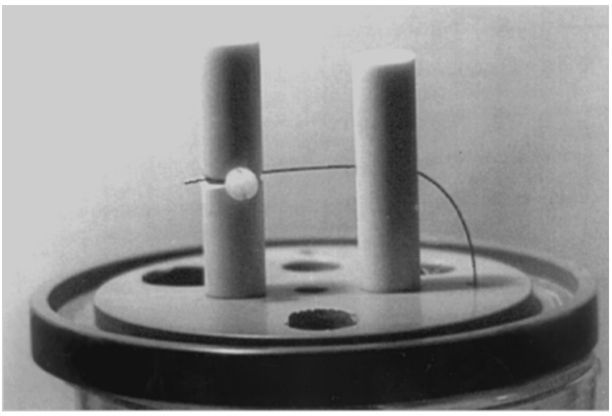

Figure 2 Specimen fixed by marcor rods with specialized wire clamps.

3. Results

3.1. Rupture potentials

In Table III all measured rupture potentials are listed. As expected, a rupture potential for the β-titanium wires (TMAI, TMAP) and the teflon-coated wires (GNTI, GSSI, FTSZ) could not be determined. Nevertheless, due to the destruction of the coating because of permanent fracture loading, corrosion may be expected for these wires under clinical conditions as well. All the other wires had rupture potentials between 187 mV and 602 mV (NHE).

3.2. SEM Analysis

3.2.1. As-received surfaces

Figs 3A–H show examples of the SEM scans of the uncoated or surface treated wires, Figs 4A–C show the examined wires with a teflon coating. All samples were measured in an as-received state. Each specimen has its own characteristic surface structure. Typical grooves caused by the production process are visible on all wires except for the teflon coated wires.

3.2.2. Wire surfaces after corrosion

Figs 5A–F show the wires examined after polarization for 10 min. Depending on the alloy under investigation,

TABLE III Rupture potentials determined for all wires in this study

Wire	Rupture potential (mV/NHE)
GBS	460
GBSI	600
DRLD	190
FTRF	350
FTG	340
FTG2	260

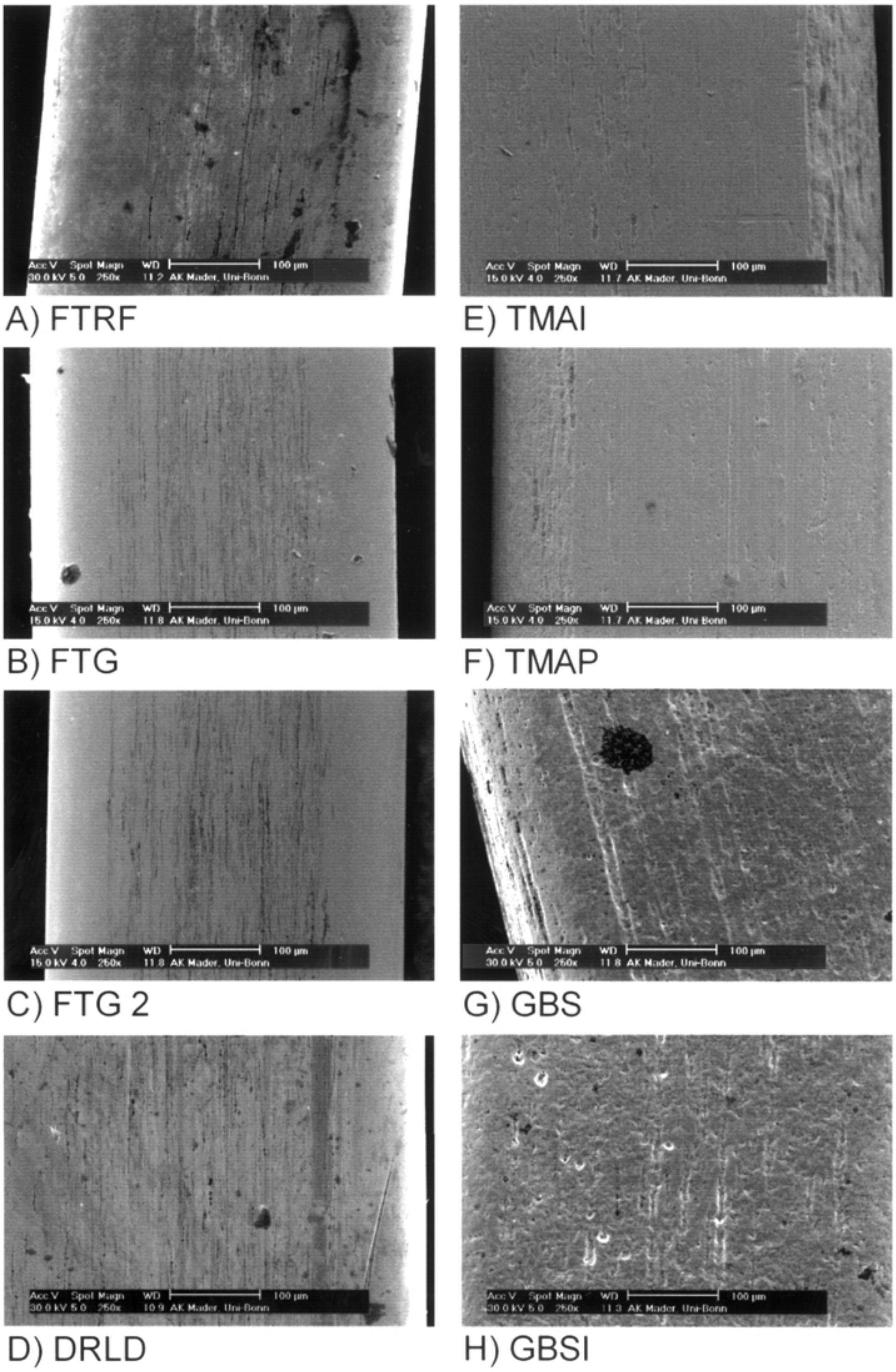

Figure 3 (A–H) Surface scans of all wires investigated in the as-received state.

corrosion appeared in different ways. In general, the surfaces of FTRF (5A) and DRLD (5D) looked quite similar after polarization, i.e. the corrosion processes seemed to be comparable. A reduction of surface destruction due to corrosion could be seen with respect to the surface modifications. From the SEM pictures it seems that corrosion defects were reduced from FTRF to FTG and FTG 2, respectively (Figs 5A, B, C) which is in contrast to the measured rupture potentials in Table III. The corrosion behavior of GBS and GBSI differed significantly from the other nickel-titanium wires in shape and position (Figs 5E, F). Corrosion defects predominantly occurred at the edges of the wires in the shape of large pits. The extent of surface destruction was reduced by ion implantation (GBSI).

3.2.3. Surface alterations after cyclic mechanical loading

After the mechanical loading tests, the wires could be subdivided into three groups. The wires of the first group (FTG, FTG 2, TMAI, TMAP and GNTI) showed no significant changes in their surface structure and the scans looked similar to the as-received figures (4B, D etc.). In the second group crystallographic changes in the structural constitution due to the mechanical stress and

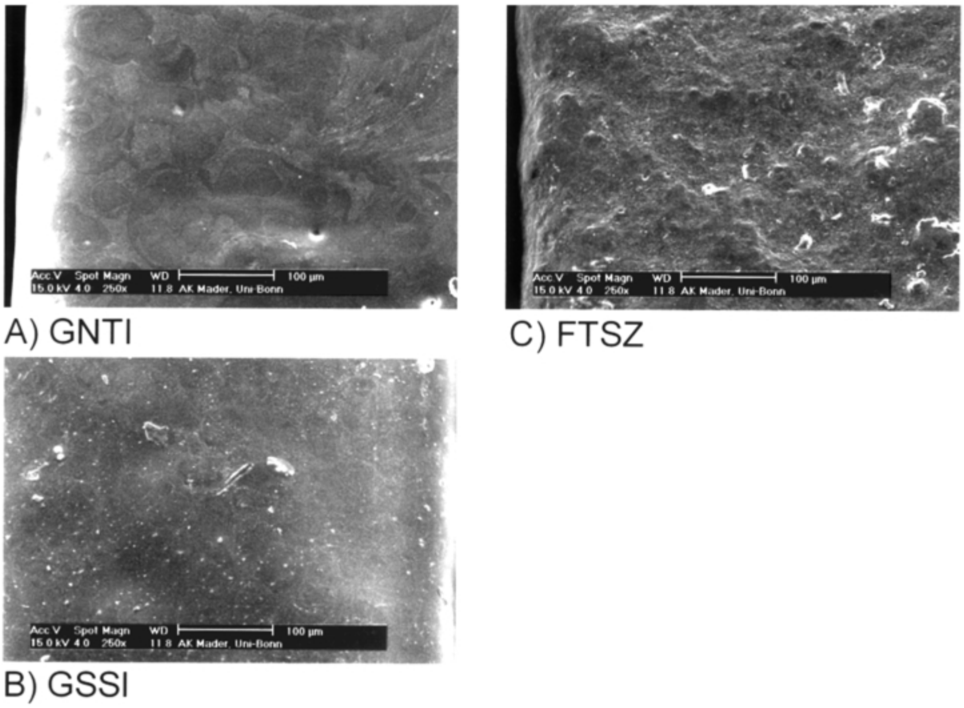

Figure 4 (A–C) As-received surfaces of the teflon-coated wires.

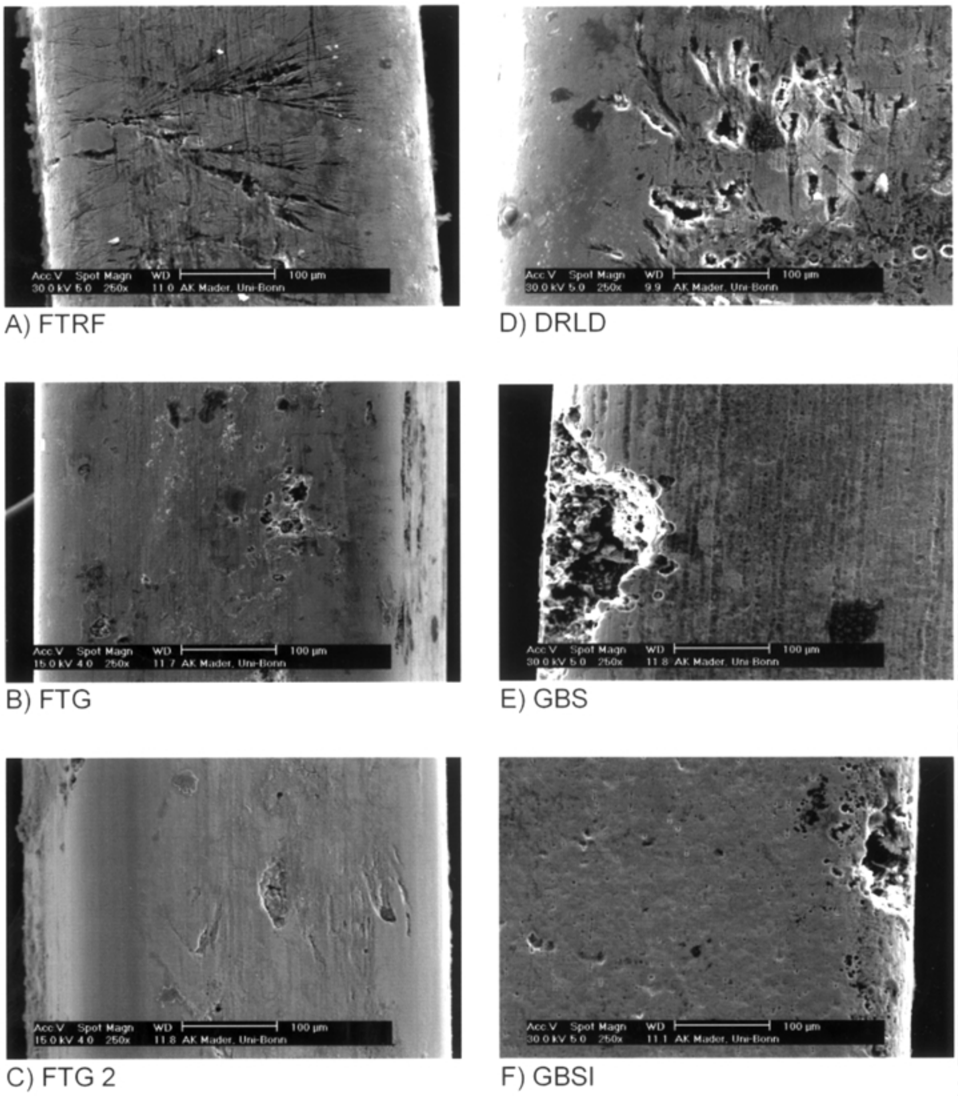

Figure 5 (A–F) Surface defects after potentiostatic loading of the orthodnotic wires. A reduction in corrosion could be achieved by surface treatment with polyethylene (wires FTRF, FTG and FTG 2 (A–B)). The untreated wires FTRF (A) and DRLD (D) show similar corrosion behavior. Treatment of the wire surface by ion implantation reduces corrosion (GBS, untreated (A) and GBSI, ion implantation (F)).

the repeatedly induced phase transformations between austenite and martensite could be observed (GBS, GBSI, FTRF and DRLD). These are documented by the dark zones in the SEM scans in Figs 6A and 6B. A change in the mechanical properties might be the consequence. The last group were the teflon coated wires FTSZ and GSSI. The damage in their surface was visible, since large parts of the coating was peeled off (Figs 6C, D).

4. Discussion

4.1. Corrosion behavior

The main objective of this study was to investigate the influence of surface modifications on the corrosion behavior of orthodontic wires. According to the SEM scans each wire has a typical surface structure resulting from different production and especially finishing processes or from coatings and surface treatments. All investigated surface modifications influenced the corrosion behavior of the orthodontic wires compared to their reference wires.

Teflon coatings suppressed corrosion processes completely. However, as surface defects of these coatings might occur during clinical use, the corrosion behavior of the core wire will become decisive after a certain interval of intra oral use. Thus, it is important to know the corrosion behavior of the original wire of that brand as well. Most of the teflon-coated wires have their uncoated counterparts from the same manufacturer, so that the clinician can consider the risk with the application of a certain wire. However, it is more reasonable to select a more corrosion resistant wire.

As expected, no rupture potentials for the β-titanium wires TMAI and TMAP could be measured, as well. This behavior is explained by the use of the highly corrosion resistant β-titanium alloy and not by the surface modification done by implantion of ions into the wire surface. The effect of ion implantation can be seen by the aid of the results for the wires GBS and GBSI. The rise in rupture potential results in corrosion processes that start at higher potentials and thus the SEM scans of these wires showed that the amount of corrosive destruction was slightly reduced by ion implantation.

The polyethylene coatings altered the corrosive behavior of the wires as well. From FTRF to FTG and FTG 2 the rupture potentials declined and corrosion should easily take place. However, this does not coincide with the surface destructions. A closer look at the surface of the FTG2 wire showed that large defects on the surface of FTRF changed to a larger number of small defects on the surfaces of FTG and FTG2. Consequently, not only is the rupture potential affected by the surface, but the kind of corrosion is affected as well.

The comparison of the laboratory results with the intra oral situation is hardly possible due to the fact that potentiostatic loads in the mouth are much smaller than under laboratory conditions. Thus, only a categorization of the samples could be achieved and the determined corrosion behavior of the products analyzed must be understood as being relative among the samples. After a pronounced destruction of the surface an increase in friction, an increase in plaque accumulation and aesthetic disadvantages can be expected. For example, individual large holes (GBS, GBSI) have less effect on friction but they offer an opportunity for the retention of plaque and food. Additionally, adverse effects on material parameters cannot be excluded.

4.2. Cyclic mechanical loading

The permanent fracture resistance of the coatings was investigated with a specialized flexure test to simulate intra oral mechanical stress. During mastication forces up to 20 N or deflections up to several millimeters may

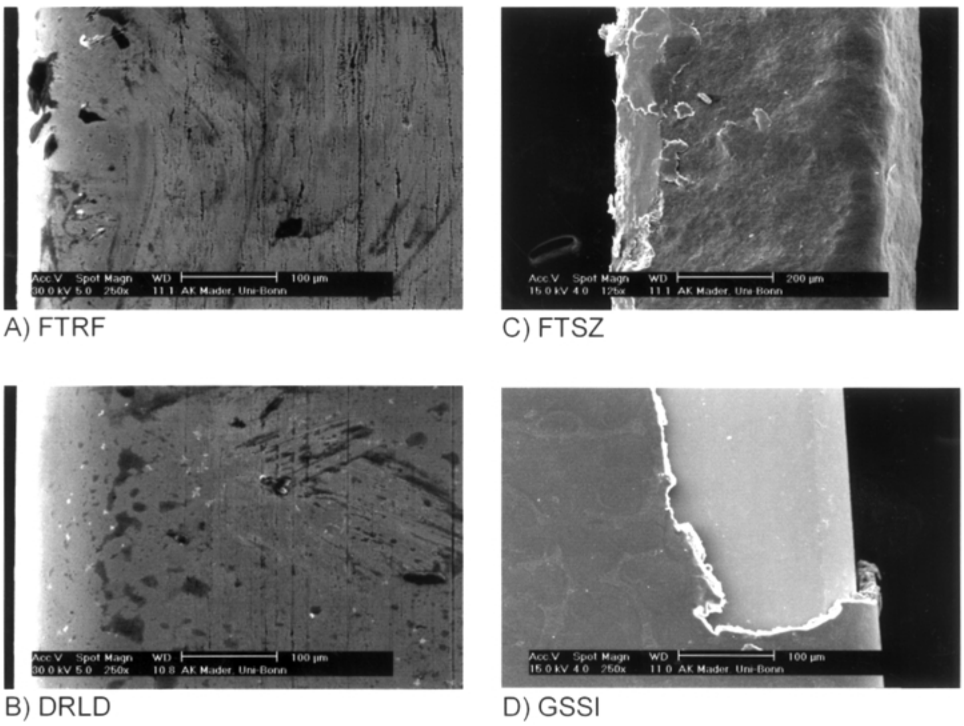

Figure 6 Surface structure after permanent mechanical cyclic loading of the orthodontic wires. Uncoated wires FTRF (A) and DRLD (B) showing a change in crystallographic structure. Destruction of the teflon coating for the wires FTSZ (C) and GSSI (D).

affect the orthodontic wire. As far as swallowing is concerned, Witt and Timper described that this activity happened 1000 to 3000 times per day [14]. In this study, the coated wires were loaded with a glass rod 5000 times. The hardness of the glass rod compares quite well with the hardness of enamel and the results should not be influenced by the use of distilled water instead of artificial saliva. These mechanical tests were performed at 37 °C, as the mechanical behavior of the NiTi alloys drastically depends on the ambient temperature. Five thousand bending cycles should be a minimum simulating the mechanical stress acting on an orthodontic wire during several weeks of intra oral application. Fracture of the wires should not occur after this number of loading cycles, whereas mechanical destructions of the wire surface or the coating can be expected [3].

Looking at the SEM pictures, the wires could be divided into different caregories. The wires of the first category showed no changes in their surface characteristics after cyclic mechanical loading. This group consisted of the polyethylene coated nickel-titanium wires FTG and FTG 2 and the teflon-coated wire GNTI. The two investigated ion implanted β-titanium wires did not show any surface alterations, too. Consequently no effect on the clinical force systems or a change in corrosion behavior of these wires should be expected. Group two was composed of the nickel-titanium wires GBS, GBSI, FTRF and DRLD. Structural changes after mechanical stress could be observed for these wires. The reason for this is a hardening of the nickel-titanium alloy, and a change in the mechanical behavior during intra oral application cannot be excluded. Group three consisted of the teflon-coated wires GSSI and FTSZ. The coating of these wires was peeled off in certain regions during the mechanical tests. This changes the properties of the wires drastically. First, corrosion processes may start at these regions and second, the sliding properties are reduced significantly, as a bracket may be hooked in the defect. Besides this, the aesthetic advantages of the white and nearly invisible teflon-coated wires are lost and plaque may be accumulated in the surface defects.

The results show that there is no direct connection between the material of the coating, the base wire and the permanent fracture and corrosion resistance. Very drastic examples are the teflon-coated wires GNTI and GSSI from the same manufacturer. The coating remained undamaged on the highly flexible nickel titanium wire while it peeled off from the stiff stainless steel wire. At the same time the teflon-coated nickel-titanium wire FTSZ showed surface defects as well. These unclear interdependencies of wire alloy, coating and mechanical and potentiostatic load mode that exist in the mouth make it difficult for the practitioner to decide which wire to select. Consequently, future studies will have to focus on corrosion and mechanical stability under clinical use of these wires.

References

1. C. BOURAUEL, T. FRIES, D. DRESCHER and R. PLIETSCH, *Eur. J. Orthod.* **20** (1998) 79.
2. W. J. BUEHLER, J. V. GILFRICH and R. C. WILEY, *J. Appl. Phys.* **34** (1963) 1457.
3. D. DRESCHER, C. BOURAUEL, W. SONNERBORN and G. P. F. SCHMUTH, *Schweiz. Monatsschr. Zahnmed.* **104** (1994) 578.
4. T. FUSAYAMA, T. KATAYORI and S. NOMOTO, *J. Dent. Res.* **42** (1963) 1183.
5. M. R. GRIMSDOTTIR, A. HENSTEN-PETTERSEN and A. KULLMANN, *Eur. J. Orthod.* **14** (1992) 47.
6. M. R. GRIMSDOTTIR, A. HENSTEN-PETTERSEN and A. KULLMANN, *Biomaterials.* **15** (1994) 1157.
7. J. GEIS-GERSTORFER and H. WEBER, *Dtsch. Zahnärztl. Z.* **40** (1985) 87.
8. R. I. HOLLAND, *Dent. Mater.* **8** (1992) 241.
9. H. F. KAPPERT, I. JONAS, M. LIEBERMANN and T. RAKOSI, *Fortschr. Kieferorthop.* **49** (1988) 358.
10. B. KRATZENSTEIN, H. WEBER, J. GEIS-GERSTORFER and P. KOPPENBURG, *Dtsch. Zahnärztl. Z.* **40** (1985) 1146.
11. R. P. KUSY, J. Q. WHITLEY, M. J. MAYHEW and J. E. BUCKTHAL, *Angle Orthod.* **58** (1988) 33.
12. J. P. MOFFA, W. D. BECK and A. W. HOKE, *J. Dent. Res.* **56** (1977) Abstr. No 107.
13. K. J. J. VREEBURG, K. DE GROOT, M. VON BLOMBERG, R. J. SCHEPER, *ibid.* **63** (1984) 124.
14. E. WITT and W. TIMPER, *Fortschr. Kieferorthop.* **35** (1974) 306.
15. F. WIDU, R. JUNKER, D. DRESCHER and C. BOURAUEL, *J. Mat. Sci. Mat. Med.* **10** (1999) 275.

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