Dental Materials (2006) **22**, 346–352

dental materials

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Effect of toothbrushing on titanium surface: An approach to understanding surface properties of brushed titanium

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Received 23 September 2004; received in revised form 23 February 2005; accepted 4 April 2005

KEYWORDS
Toothbrushing;
Dentifrice;
Titanium;
Surface texture;
Surface composition;
Abrading chips

Summary *Objectives*. This in vitro study aimed to characterize the surface morphology and composition of toothbrushed titanium casting and thereby to elucidate interactions between the metal and abrasive material in dentifrice.

Methods. Specimens were cast from CP Ti ingots and then mirror-finished. Two fluoride-free toothpastes containing crystalline $CaHPO_4 \cdot 2H_2O$ and amorphous SiO_2 particles as abrasive were slurried with distilled water (15 g/30 mL). While toothbrushes were reciprocated at 120 strokes/min for 350,400 strokes, the specimens were brushed with the respective slurries under a load of 2.45 N. The brushed and non-brushed surfaces were characterized by means of SPM, EPMA, and XPS. SPM data were analyzed using one-way ANOVA, followed by post hoc Tukey test ($p < 0.01$).

Results. Irrespective of toothpastes, toothbrushing had a significant influence on surface roughness. The $CaHPO_4 \cdot 2H_2O$-containing paste produced much rougher surface than the SiO_2-containing paste. Both the surfaces were chemically altered due to reactions with the respective abrasive materials. Abrading chips had dimensions of micron to submicron order. A number of chips were attached to abrasive particles.

Significance. The alterations of surface morphology and composition may affect biological responses of titanium in the oral environment. Dentifrice with lower abrasivity might be advisable for daily oral hygiene practice of patients with dental titanium devices.

Introduction

Clinical applications of titanium in medical and dental practices have been often documented with a great attention on its excellent biocompatibility.

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doi:10.1016/j.dental.2005.04.026

With the development in dental casting technique for titanium, the metal has been used for crowns, fixed and removable partial denture frameworks, and implant frameworks [1]. Orthodontic brackets made up of pure titanium have been well accepted [2], especially for patients with allergy to nickel and other specific substances [3]. The distinguished biocompatibility of titanium is mainly attributed to the surface oxide film that has excellent resistance to corrosion. However, the main drawback is poor resistance to wear.

Dentifrice includes different abrasives, which are basically used to clean dental plaque, pellicle, and food debris from the teeth. However, restorative materials undergo mechanical degradation due to the abrading action of dentifrice [4]. In the long term, the abrasion effect causes biological disadvantages, such as accumulation of dental plaque [5] and increased element release associated with toxicity [6].

Most of the studies relating to dentifrice effects on titanium surface have been involved in the corrosive action of fluoride added to toothpaste [7, 8]. However, taking the corrosion aspect into account, Siirilä and Könönen [9] had claimed that the abrasion caused by toothbrush bristles, rather than the effect of additive fluoride (0.125%), was the main deteriorating factor for titanium. The personal dental hygiene procedure with brush has been reported to produce superficial grooves on the titanium implant abutments [10]. On the contrary, Johannsen et al. [11,12] reported that toothbrushing with toothpaste rendered polishing effect to titanium surface.

On the other hand, abrading and polishing processes of titanium brought about mechanical surface disturbance accompanied by alteration of surface composition [13,14]. Such surface disturbance and resultant chemical alteration were also expected to occur during toothbrushing with dentifrice. The chemically altered surface may have biological responses other than that have been believed for titanium with spontaneous oxide film. Therefore, brushed titanium surface needs to be chemically characterized from the viewpoint of long-term biocompatibility. Nevertheless, no studies have evaluated the surface composition of titanium brushed with dentifrice.

This in vitro study was designed to investigate the effect of toothbrushing on surface morphology and composition of titanium and thereby to elucidate interactions between the metal and abrasive material in toothpaste. The brushed surfaces were characterized by means of scanning probe microscopy (SPM), secondary electron (SE) microscopy, electron probe microanalysis (EPMA), and X-ray photoelectron spectroscopy (XPS). Abrading chips in the toothpaste used were also examined by element analysis.

Materials and methods

Preparation of specimens

Specimens were cast titanium plates of 15 mm in width, 35 mm in length, and 1.5 mm in thickness. In a dental titanium-casting unit (Autocast HC-III, GC, Japan), CP titanium ingots (T-alloy M, GC, Japan), equivalent to Grade 2 classified in Japan Industry Standard, were cast into room temperature mold made from a phosphate-bonded investment (Titavest II, Ohara, Japan). On a polishing machine (AUTOMAX, Refine Tec, Japan), both wide sides of cast plates were progressively ground with waterproof abrasive papers of SiC under running tap water, and finally up to #1000 grit. Final polishing was performed on a buffing cloth (OP-NaP, Struers, Denmark) using colloidal silica (0.06 μm and pH 9.8) (MASTERMET, Buehler, USA), followed by ultrasonic cleaning in alcohol. At last, the thickness of cast specimens was reduced from 1.5 to approximately 0.7 mm. Hence, the grinding and polishing procedures completely removed the surface reaction layers [15] resulting from reactions with investment material components.

Preparation of toothpaste slurry

Two fluoride-free toothpastes (New Salt A, Sunstar, Japan; Etiquette Lion, Lion, Japan) were selected so that fluoride-induced corrosion would not influence the experimental results [7–9]. They will be denoted by NSA and ETL, respectively. The respective pastes of 15 g were mixed with distilled water of 30 mL. The pH values of the prepared slurries were 7.8 and 9.8, respectively.

Brushing test

Specimens were fixed in the trough attached to a toothbrushing wear testing machine (K706, Tokyo Giken, Japan). The trough was loaded with 45 mL slurry. A toothbrush (Dent EX 33 soft, Lion, Japan), whose bristle transplanted portion was 20 mm in length and 6 mm in width, was automatically reciprocated over a stroke of 10 mm and at 120 strokes/min for 350,400 strokes. In the meantime, specimens were brushed under a load of 2.45 N at room temperature. The brush was changed in the middle of brushing test. Precautions were taken so that specimens would be free from any galvanic corrosion effects. After being brushed, specimens were rinsed with distilled water, ultrasonically cleaned in alcohol for 15 min, and finally dried by air blow.

SPM

SPM analysis was conducted to evaluate surface roughness (JSPM-4210, JEOL, Japan). Three specimens were prepared for each condition. As-mirror polished specimens were used as control. Three areas of 50 μm square were randomly chosen on each specimen. Each area was scanned in tapping mode. Centerline average roughness (Ra) values were computed along five horizontal lines randomly chosen on the individual areas. For each condition, the arithmetic mean of Ra and standard deviation were calculated from the 45 ($3\times3\times5$) measurements. The effect of toothbrushing on the surface roughness was tested by one-way ANOVA. Post hoc Tukey test was conducted to compare the means of the test groups ($p<0.01$).

EPMA

Morphological comparison of brushed surfaces was made by SE image observation (EPMA-8705-HII, Shimadzu, Japan). For distributions of Ca, P, Si, and O, the area corresponding to the SE image was analyzed in sample stage scanning mode (scanning step = 1 μm).

For dissolution of soluble salts, a certain volume of each fresh paste was repeatedly diluted with distilled water and finally air-dried. Abrasive particles in the dried powder sample were morphologically observed through SE image. Similarly, each sample was prepared from the respective pastes used. Abrading chips in the sample were examined by element analysis.

XPS

The chemical bond states of elements present in brushed surfaces were elucidated by XPS analysis using an exiting source of monochromated Al K_α (QUANTUM 2000, ULVAC-PHI, Japan). After wide survey scan, Ca*2P*, P*2P*, Si*2P*, and Ti*2P* spectra were acquired by high-resolution scan. Since electrostatic surface charging leads to unexpected shift of binding energy peak, a neutralization ion gun attached to the spectrometer was operated during analysis. The analyzed area was 100 μm in diameter and the take-off angle was 45°. The analyzing chamber was held at higher vacuum than 1.33 μPa.

Ar^+ ion sputter etching and XPS analysis were alternately repeated and depth profiles of Ca*2P*, P*2P*, Si*2P*, and Ti*2P* spectra were thereby determined. The sputtered area was 2×2 mm^2. Specimen was rotated during sputtering so that the influence of surface roughness on the profiles could be minimized. The sputtering rate was calibrated to be 0.36 nm/min for SiO_2 as reference.

Abrasive particles in each fresh paste were collected according to the above-mentioned procedure and then subjected to XPS analysis. Thereby, Ca*2P*, P*2P*, and Si*2P* spectra were obtained as reference.

Results

Surface roughness

As compared with the control, toothbrushing significantly increased the surface roughness (Fig. 1). NSA produced a significantly rougher surface than ETL.

Surface morphology and composition

NSA produced very sharp hairline scratches along the brushing direction (Fig. 2a). Ca and P appeared to non-uniformly distribute corresponding to the hairline pattern. In contrast, a number of dimples, as well as slightly visible grooves, were dispersed on ETL-brushed surface (Fig. 2b). Si appeared to non-uniformly distribute depending on the dimple pattern. Similarly, oxygen maps (not shown) of both surfaces showed non-uniform distributions corresponding to the respective abrasion patterns. The observed non-uniformity might partly result

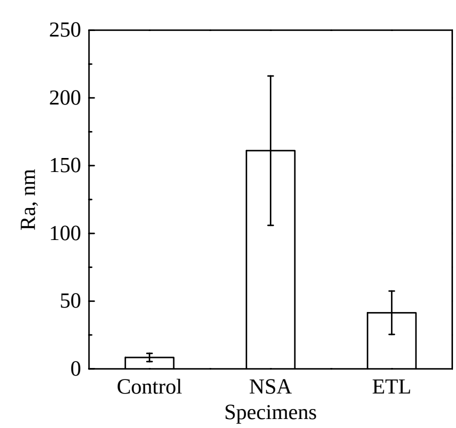

Figure 1 Results of SPM. Centerline average roughness values, Ra are compared among as-polished, NSA-brushed, and ETL-brushed surfaces.

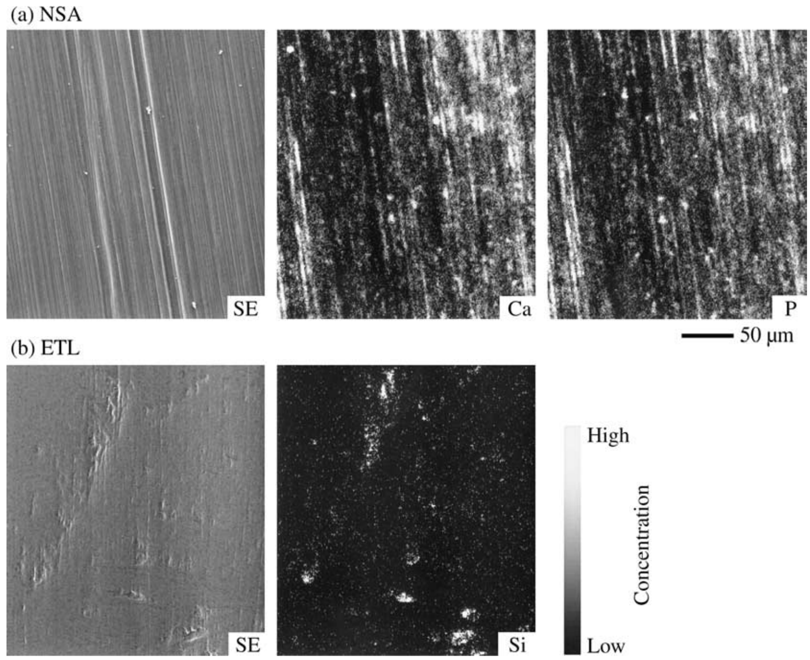

Figure 2 EPMA results of NSA-brushed (a) and ETL-brushed (b) surfaces. Representative morphology images and corresponding element maps are shown.

from surface morphology, as the directions normal to abraded slopes were different from point to point with respect to the location of each element detector.

In summary, SPM and EPMA results demonstrated that brushing with toothpaste significantly roughened surface and correspondingly altered surface composition.

Abrading chips

Titanium-rich particulates with dimensions of micron to submicron order were found in the slurries used (Fig. 3). Particulates originating from coloring agent (TiO_2) in ETL existed in isolated state. The other particulates, most of which were attached to abrasive particles, were chips abraded from the brushing surface. Similar results were observed in NSA slurry used.

Chemical bond state of elements in surface

Ca2*p* and P2*p* peaks from NSA-brushed surface were located on higher binding energy side than the respective reference peaks (Fig. 4). Both the peaks became low with increasing sputtering time. But they had a trace of peak even at the last time when Ti2*p* spectrum almost corresponded to metallic titanium. P2*p* spectra suggested the presence of a trace amount of compound similar to TiP in the deep region (arrow in Fig. 4).

Si2*p* peak from ETL-brushed surface appeared on lower energy side than the reference peak (Fig. 5). At 8 min sputtering, the peak almost disappeared, when Ti2*p* profile had still two peaks corresponding to titanium oxides and metallic titanium.

XPS results indicated chemical alterations of brushed surface. The alterations appeared to extend much more deeply for NSA than for ETL. This difference might be mainly related to the

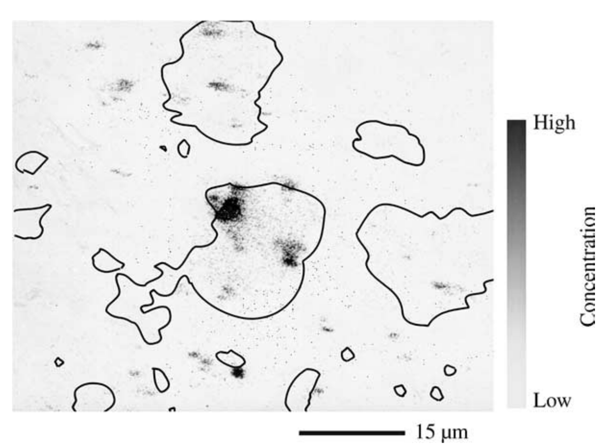

Figure 3 Titanium-rich particulates and abrasive particles in ETL slurry used. Ti map was superposed with the contour lines of abrasive particles depicted from Si map.

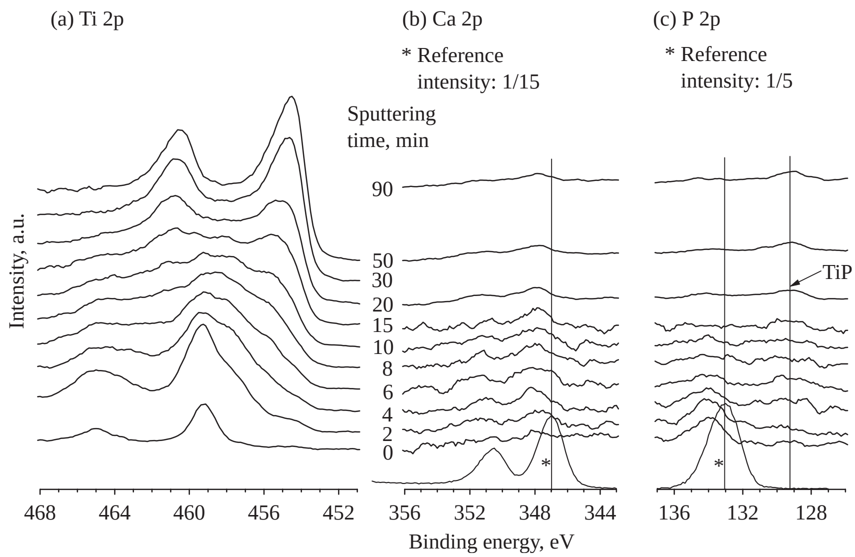

Figure 4 XPS depth profiles from NSA surface. The respective reference spectra were displayed 1/15 and 1/5 times, respectively.

difference in surface roughness between NSA and ETL.

Discussion

Although dental restorations or prostheses are exposed to daily toothbrushing throughout their service life, the present study conducted continuous brushing test for 48 h. The number of strokes (350,400) is equivalent to 2-min brushing per session, twice a day for 2 years and 8 months according to brushing scheme of Wataha et al. [6]. This period represents a long-term challenge of dental casting alloys to the mechanical disturbance from toothbrushing. In general, brushing force varies widely from person to person, regardless of toothbrush bristle stiffness. The applied force (2.45 N) is in accordance with the normal magnitude measured in a clinical study [16].

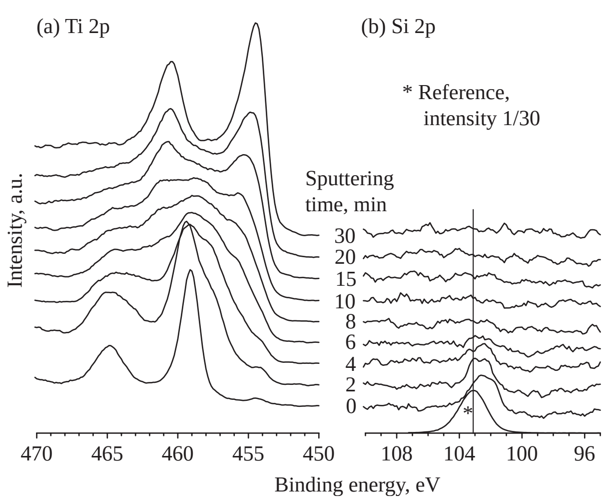

Figure 5 XPS depth profile from ETL surface. The reference profile was displayed 1/30 times.

Two toothpastes were selected with a focus on abrasive material. NSA and ETL contained crystalline $CaHPO_4 \cdot 2H_2O$ and amorphous SiO_2 particles, respectively, as confirmed by element analysis and X-ray diffraction. Both abrasives substantially abraded and significantly roughened titanium surfaces. This result was seemingly contrary to that of Johannsen et al. [11,12] who found somewhat smoothing effect after brushing with toothpastes. The contradictory results may come from the difference in starting roughness between both specimen surfaces, i.e. comparatively rough surface obtained by conventional polishing vs. smooth surface obtained by experimental mirror-polishing.

The variation of surface roughness with position was much greater than that with specimen. Thus, the present statistic analysis took account of the former rather than the latter. In other words, the mean for each condition and standard deviation were determined from the 45 measurements from three specimens, and compared by post hoc Tukey analysis. NSA-brushed surface exhibited significantly rougher texture than ETL-one (Fig. 1). The abrasion patterns were also different (Fig. 2). These results were principally due to the difference in shape and size between the respective abrasives. Indeed, NSA included large irregular particles with sharp edges (Fig. 6). On the other hand, ETL

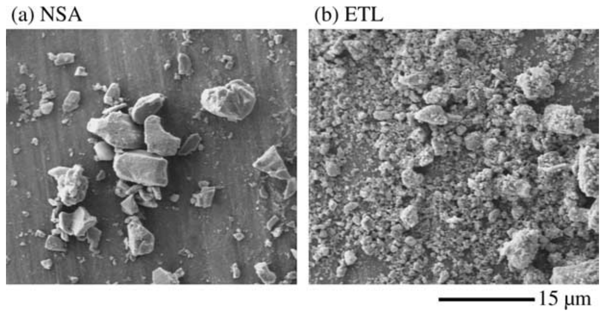

Figure 6 Abrasive particles in toothpastes non-used.

contained small round particles and relatively large spongy particles. The latter particle looked like a coagulation body of small particles.

In abrading or polishing, abrasive materials such as Al_2O_3 and Fe_2O_3 alter the surface composition of titanium [13,14]. Abrasive material mechanically destroys the protective oxide film and comes into direct contact with native titanium that is inherently reactive with most elements. Resultantly, certain reaction products are left in the oxide film that is regenerated immediately after the film destruction. This hypothetic inference was consistent with the present results of EPMA indicating the presence of abrasive-constituent elements in brushed surfaces (Fig. 2). Therefore, whether titanium similarly reacted with the abrasive materials during brushing was explored by XPS. In wide survey spectra (not shown), the major elements included Ca, P, and O from NSA-brushed surface, and Si and O from ETL-one, as expected from EPMA results. High-resolution spectra of Ca2*p*, P2*p*, and Si2*p* distinctly showed their chemical shifts in comparison with the respective references (Figs. 4 and 5).

Since the colloidal silica used as polishing agent contained the same element (silicon) as ETL paste, it was conceivable that the silica affected the EPMA and XPS results of ETL. However, a previous study [17] reported that the silica produced a chemically clean mirror surface, in which EPMA failed to detect silicon. Although the XPS-level outermost surface had been slightly silicon-contaminated, the toothbrushing continued the renewal of surface, hence removing the silicon contamination. The calcium, phosphorus and silicon that were analyzed in the present study came from the abrasives in toothpastes. Therefore, it is concluded that, as far as titanium is concerned, the embedment of abrasive particles into brushing surface does not play the major role in the alteration of surface composition. Probably, reactions of titanium with the abrasive materials yield compounds in the regenerated oxide film: Ti–O–Ca–P for NSA and Ti–O–Si for ETL. However, exact chemical formulas of these compounds were still left undetermined.

The effects of morphological and chemical alterations on the biocompatibility of titanium should be investigated in vivo in detail. Nonetheless, it has been reported that rough surface harbors 25 times bacteria as many as smooth surface [18]. Therefore, NSA-brushed surface with rough texture may favor the accumulation of bacteria. Moreover, surface modification of titanium by calcium ion incorporation enhances salivary protein adsorption on the treated surface [19], which facilitates the attachment of oral bacteria [20]. It is probable that the bacterial plaque accumulation is considerably promoted on titanium surface brushed with toothpaste containing calcium phosphate.

As stated previously, the destruction of oxide film by abrading agent is instantly followed by the spontaneous recovery of oxide film through reoxidation reaction. However, it takes a time for the regenerated film to attain to a stable state [21]. While exposed substrate titanium is not protected from dissolution, titanium ions are released in the oral environment. The chemical state of released titanium ion is not fully known. However, elements released from prostheses are supposed to be absorbed in the gastrointestinal tract, respiratory system, and oral mucus membrane [22].

Brushing also released abrading chips with dimensions of micron to submicron order into the toothpaste slurry (Fig. 3). A number of chips were attached to the abrading agent that has strong chemical affinity with titanium. Moreover, the surface of chip may have a chemical structure similar to that of brushed surface. However, the present study was not able to chemically characterize the chip surface.

The size and concentration of titanium wear particle influence cellular responses [23]. Titanium particulate smaller than cell, which is around 10 μm in size, causes cytotoxic reaction in vivo and in vitro [24]. Particulate titanium also induces genomic instability in human fibroblast [25]. Therefore, it may be assumed that some of released titanium ions, abrading chips, as well as abrasive-constituent elements are absorbed in the human body, eventually leading to the occurrence of adverse effects. The effects of these substances on the human body need to be further investigated, particularly in relation to metallic allergy.

Although this is an in vitro study, it is clear that toothbrushing of titanium results in alterations of surface morphology and composition as well as in release of particulate chips. The degrees of these occurrences depend on abrasive agent contained in toothpaste. Dentifrice with lower abrasivity may be advisable for patients with dental titanium devices.

Conclusions

Within the limitations of this study, the following conclusions were made:

1. Titanium surface was differently abraded and roughened depending on the abrading agent in toothpaste.
2. The surface composition was altered probably because of reactions with the abrasive material.
3. Particulate abrading chips were attached to the abrasive agent.

Acknowledgements

Part of this research was supported by Grant-in-Aid for Scientific Research (#14571842) from the Ministry of Education, Science, Sports and Culture of Japan. The authors are grateful to Mr M. Kobayashi, operator of EMX Laboratory, Niigata University Center for Instrumental Analysis, for his helpful suggestion and assistance in element analysis.

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