Hydrogen content in titanium and a titanium–zirconium alloy after acid etching

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ABSTRACT

Dental implant alloys made from titanium and zirconium are known for their high mechanical strength, fracture toughness and corrosion resistance in comparison with commercially pure titanium. The aim of the study was to investigate possible differences in the surface chemistry and/or surface topography of titanium and titanium–zirconium surfaces after sand blasting and acid etching. The two surfaces were compared by X-ray photoelectron spectroscopy, secondary ion mass spectroscopy, scanning electron microscopy and profilometry.

The 1.9 times greater surface hydrogen concentration of titanium zirconium compared to titanium was found to be the major difference between the two materials. Zirconium appeared to enhance hydride formation on titanium alloys when etched in acid. Surface topography revealed significant differences on the micro and nanoscale. Surface roughness was increased significantly ($p < 0.01$) on the titanium–zirconium alloy. High-resolution images showed nanostructures only present on titanium zirconium.

1. Introduction

A screw-shaped dental implant is designed to transfer the load to the jawbone, replacing the root of a tooth. It should distribute the occurring forces homogeneously into the surrounding bone tissue. High mechanical strength and fracture toughness as well as biocompatibility are essential for this application. Thus today's dental implants are mostly made from titanium (Ti) or its alloys, as they provide those features. Titanium and zirconium are known for their outstanding biocompatibility. When these materials are placed in bone, the body forms a bonelike apatite layer, which enhances bone-to-implant contact [1]. The bone tissue response of dental implants is governed by several factors. Various studies have shown the importance of surface chemistry and surface morphology for biological response [2,3].

Optimization of the surface roughness is one approach to improve bone healing, using mechanical and chemical methods or a combination thereof [4–9]. Blasting and etching have shown successful results in optimizing surface roughness for improved bone response [10–14]. Studies showed that rough implant surfaces promote osseointegration and biomechanical fixation better than smooth surfaces. A surface roughness (S_a) in the range of 1–4 μm is believed to be optimal for providing a stable interface between mineralized bone and the surface of the implant [12,13,15,16].

Chemical modification of the surface is another route to enhance the bone's response to dental implants. Titanium builds up a native oxide layer in the presence of oxygen. The oxide layer increases the corrosion resistance of titanium. As a result, titanium is inert in the human body [17]. Modification of the oxide layer by anodic oxidation is one of multiple approaches to change the surface chemistry of titanium. Although oxide layer thickness could be increased more than tenfold, hard tissue healing hardly improved [18–20]. In search of a more reactive surface, acid etching was found to be preferable. Increased surface hydrogen levels have been reported for titanium after sand blasting and acid etching (SBAE) [21,22]. Improved clinical performance has been reported for SBAE surfaces [23]. Besides acid etching, cathodic reduction in an acidic solution was shown to successfully increase surface hydrogen as well [24,25]. Etching in hydrofluoric acid (HF) also elevated surface hydrogen and fluoride [26]. Dental implants with fluoride doped titanium dioxide showed enhanced osteoblast differentiation and bone growth [16,27,28]. The surface energy and wettability of SBAE surfaces can be further enhanced by reducing environmental carbon contamination. Handling under protective cover gas and storage in saline solution are effective methods of surface carbon reduction [29,30]. Titanium hydride appeared not only to influence the surface's clinical performance but also opens new methods of surface modification. Shih et al. used nanostructured titanium hydride created by cathodization to form a nanoporous oxide layer by anodization [31]. Hydride appeared to be essential in forming this nanostructured surface. Recent studies have suggested a possible relation between a surface's hydrogen content and its in vivo performance [23,32].

Previous studies showed that a titanium–zirconium (TiZr) alloy induced similar or even better bone tissue response compared to titanium with the same sand blasted and acid etched (SBAE) surfaces [33,34]. TiZr alloys also showed increased fracture toughness and corrosion resistance over commercially pure titanium [35,36]. This allows the production of implants with smaller diameters that are more suitable for use in critical implantation sites, such as in the front of the lower jaw where bone is scarce and the crestal bone is thick [34].

The aim of this study was to investigate possible differences in the surface chemistry and/or surface topography of sand blasted and acid etched titanium (Ti SBAE) and titanium–zirconium (TiZr SBAE) coin-shaped samples. Both surfaces were compared by XPS (X-ray photoelectron spectroscopy) and SIMS (secondary ion mass spectroscopy) for differences in surface chemistry. In addition, FE-SEM (field emission scanning electron microscopy) and profilometry were applied to detect differences in surface morphology or roughness.

2. Material and methods

2.1. Samples

This study used grade IV titanium (Ti) and a titanium–zirconium alloy (TiZr) containing 13% to 17% zirconium [35]. Surfaces were sand blasted with large-grit (0.25 mm–0.5 mm) aluminum oxide particles and acid etched in a mixture of hydrochloric and sulfuric acid at 125 °C–130 °C for 5 min (SBAE). The samples were handled under nitrogen cover gas and stored in 0.9% NaCl solution to obtain a surface comparable with the commercially available SLActive® surface (Institut Straumann AG, Basel, Switzerland). This surface modification has been previously described in other studies [22,29]. Machined surfaces of both materials (Ti and TiZr) were only used as a control in the SIMS analysis. Coin-shaped samples with a diameter of 4.39 mm and a height of 2 mm were used in this study.

2.2. Chemical analysis

Secondary ion mass spectroscopy (SIMS) was used for obtaining depth profiles of the ^1H, ^{18}O, ^{46}Ti and ^{50}Ti isotopes. Analysis was performed on an IMS 7f (Cameca, Paris, France) magnetic sector SIMS. All samples were analyzed at 20 °C using a 50 nA primary beam of 15 keV Cs^+ ions. The sputtered surface area measured 200 μm × 200 μm and all secondary ions were collected from the central part of the crater measuring 67 μm × 67 μm. Count intensity (c/s) of a measurement is equivalent to the relative concentration of an isotope. For improved illustration and comparability to other studies a depth scale (μm) was added to the figures by relating the depth of the crater to the maximum sputtering time [9,24]. Although, the sputtering rate of the material was likely not a linear function of the crater depth, the depth in μm was given based on the assumption of a linear sputtering rate. The total amount of an isotope was assessed by integrating the count intensity over the depth of a measurement. The layer thickness was assessed by approaching the zero slope of a depth profile as a lower limit.

The XPS analysis was carried out on an Axis Ultra^{DLD} XP spectrometer (Kratos Analytical Limited, Manchester, United Kingdom). The instrument resolution was 1.1 eV for the survey scans and 0.55 eV for the detail scans for the employed settings, determined by measuring of the full width at half maximum FWHM of the Ag 3d5/2 peak obtained on sputter cleaned silver foil. The emission of the photoelectrons from the sample was 90° (normal to sample surface), and the incidence angle of the X-rays was 33.3° (or 56.7° between X-ray incidence direction and captured photoelectron emission direction). For the survey spectra, a hybrid lens mode was used with slot aperture at 80 eV pass energy. The survey scan was executed at between 0 eV and 1100 eV binding energy. For the detail spectra, a hybrid lens mode with slot aperture was used at a pass energy of 20 eV. Detail spectra were recorded for O1s, C1s, Ti2p, N1s and Zr3d. The energy shift due to surface charging was below 1 eV based on the C 1 s peak position relative to the established BEs, therefore the experiment was performed without charge compensation.

2.3. Surface characterization

A PLμ 2300 (Sensofar-Tech S.L., Terrassa, Spain) blue light laser profilometer and interferometer using a 50× EPI (Nikon, Tokyo, Japan) confocal objective was used for assessing an extended topography of 2×2 images. Each had a viewing area of 253 μm × 190 μm at 20% overlapping. Eight images of each material were analyzed. The advanced topography software Sensomap 4.1 Plus (Sensofar-Tech S.L., Terrassa, Spain) for dimensional and surface state metrology was used to process the measured data. The same profilometer was used for measuring the actual depth of the SIMS crater.

The following surface amplitude parameters were analyzed to compare the materials: average roughness (S_a), total height of the surface (S_t), skewness of the height distribution (S_{sk}), kurtosis of the height distribution (S_{ku}), maximum height of summits (S_p) and maximum depth of valleys (S_v), the functional parameters as valley fluid retention index (S_{vi}) and core fluid retention index (S_{ci}) and the special parameter density of peaks between two levels (S_{Pc}).

All SEM images in this study were taken by a Quanta 200 FEG (FEI Hillsboro, Oregon, USA) field-emission SEM (FE-SEM). Its Schottky field emission gun (FEG) allowed high spatial resolution. All samples were sputtered with platinum for one minute prior to imaging and mounted on the sample holder with conductive carbon tape.

2.4. Statistical analysis

Data were compared using a two-way ANOVA in SigmaPlot 11 (Systat Software, San José, California, USA). A normality test was performed; once this was passed, all samples were compared in pairs using the Holm–Sidak method. ANOVA was performed on ranks when the normality test failed, using the Tukey test. The data were displayed as arithmetic mean values with standard deviation when the data were distributed normally and as median values with interquartile range when the data were not distributed normally.

3. Results

3.1. Surface chemistry

Depth profiles taken for hydrogen (^1H) (Fig. 1A) revealed substantially higher maximum hydrogen concentration and total hydrogen amounts for sand blasted and acid etched (SBAE) samples when compared to machined reference samples. SBAE surfaces also showed hydrogen layers more than ten times thicker than for machined surfaces. Table 1 shows the total hydrogen amount, concentration and layer thickness. When comparing SBAE surfaces of both materials, TiZr SBAE showed a hydrogen concentration 1.9 times higher than Ti SBAE. Moreover, Ti SBAE showed the highest hydrogen concentration at 0.16 μm, and TiZr SBAE showed the highest concentration at 0.1 μm below the surface. The hydrogen layer thickness of TiZr SBAE was found to be over 1 μm thicker than for Ti SBAE.

Oxygen (^{18}O) depth profiles (Fig. 1B) revealed increased oxygen concentration, total amount and layer thickness for SBAE surfaces compared to machined surfaces. While machined surfaces showed almost identical oxygen depth profiles for both materials, SBAE surfaces differed significantly. TiZr SBAE had significantly lower total oxygen and a thinner layer than Ti SBAE. The oxygen concentration did not show significant differences.

Depth profiles of two titanium isotopes, ^{46}Ti and ^{50}Ti, were chosen as a control for the titanium layer. The ^{46}Ti isotope's depth profile (Fig. 1C) showed a clear correlation to the ^{18}O isotope's (Fig. 1B). Its