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Hydrofluoric acid etching of dental zirconia. Part 2: effect on flexural strength and ageing behavior

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ABSTRACT

Among the diverse treatments proposed to promote the osseointegration of zirconia dental implants, hydrofluoric acid (HF) etching appears to be a good candidate. However little is known on the effect of this process on the mechanical properties and long-term reliability. In this work, the surface integrity, the flexural strength and the ageing sensitivity of yttria-stabilized zirconia were assessed after etching in HF 40%. Results show that etching induces an increase of monoclinic phase content and a decrease in flexural strength. The strength decrease is limited to 15% for etching times below 60 min, whereas it reaches 29% after 120 min because of the formation of large etching pits. No substantial change in the ageing sensitivity was evidenced. Within the limits of this study, HF 40% etched zirconia appears to be reliable for long-term implantation provided that the etching duration does not exceed 60 min.

1. Introduction

Yttria-stabilized tetragonal zirconia polycrystals (Y-TZP, short: zirconia) are biocompatible and exhibit the best combination of strength and toughness of single-phase oxide ceramics. They were introduced as biomaterials in the end of the 1980s to overcome the limitations of alumina in the field of orthopedics [1]. Their excellent mechanical properties are due to phase transformation toughening: under stress the metastable tetragonal grains at the crack tip transform into monoclinic phase with a volume expansion, and this induces compressive stresses on the crack [2]. Unfortunately, the phase transformation is also the cause of their main weakness: in the presence of water the tetragonal phase can transform spontaneously, inducing micro-cracks and a loss of integrity of the material (see for instance the review from Lawson [3]). The impact of this phenomenon, known as Low Temperature Degradation (LTD) or ageing, was thought to be limited in vivo until 2001, when 400 Prozyr® femoral heads failed in a very short period because of accelerated LTD [1]. This unfortunate event highlighted that minor changes in the fabrication process of zirconia ceramics may induce a dramatic increase of ageing sensitivity and that any modification should thus be followed by a careful assessment of its impact on long-term reliability.

While monolithic zirconia has been almost abandoned for orthopedic applications, in the last decade its use in restorative dentistry has been growing fast [4]. In particular, its good esthetics, high resistance to corrosion and the absence of allergic reaction make zirconia a good candidate to replace titanium for the fabrication of dental implants [5]. However, some authors reported a higher failure rate and a higher marginal bone loss when comparing zirconia to titanium. According to them, the use of zirconia implants does not appear recommendable at the moment except for specific cases (e.g. allergy to titanium), and there is a need for further research before generalizing their clinical use [6,7].

To solve the problem of bone loss mentioned above, the key is to achieve a good osseointegration, which was shown to be promoted by rough surfaces [8]. Among the different surface chemical treatments already proposed in the literature for this purpose, hydrofluoric acid (HF) etching appears to be a good candidate [9–12]. Besides zirconia dental implants with acid etched surface are already commercialized (CeraRoot implants with ICE™ surface) and apparently have shown a similar success rate as compared to titanium implants after five years of follow-up study [13].

Despite the Prozyr® failure event, the dental industry may not have been sufficiently concerned with the problems related to age-

Abbreviations: DI water, deionized water; FIB, focused ion beam; HF, hydrofluoric acid; LTD, low temperature degradation; SEM, scanning electron microscopy; Y-TZP, yttria-stabilized tetragonal zirconia polycrystals; 3Y-TZP, 3 mol% Y-TZP.

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Table 1
Names of the different groups of samples and description of the associated treatments.

Group	Description of the treatment
Control	No treatment (polished surface)
HF40-30	Immersed 30 min in HF 40%
HF40-60	Immersed 60 min in HF 40%
HF40-120	Immersed 120 min in HF 40%
Control-Aged	Polished and aged
HF40-30-Aged	Immersed 30 min in HF 40% and aged
HF40-60-Aged	Immersed 60 min in HF 40% and aged
HF40-120-Aged	Immersed 120 min in HF 40% and aged

ing [1,14]. As a result, as far as the authors know, there is currently no study of the effect of acid etching on the long-term reliability of dental zirconia. The objective of this work is therefore to address this lack of knowledge by assessing the impact of HF etching on the surface integrity, the flexural strength and the ageing sensitivity. The surface characterization and the questions related to the etching mechanism are treated in a separated article [12].

2. Materials and methods

2.1. Zirconia disks preparation

Commercial 3Y-TZP powder (TZ-3YSB-E Tosoh Co., Japan) was cold isostatically compacted under pressure of 200 MPa in a cylindrical mold for producing a green body, and then sintered in an alumina tube furnace at 1450 °C for two hours (3 °C/min heating and cooling rates). The sintered ceramic cylinders were cut into specimens in the form of disks (2 mm thick, 9 mm diameter), which were ground and polished down to a 3 μm diamond suspension. The samples were then successively cleaned for five minutes with acetone, ethanol and deionized water (DI water) in an ultrasonic bath in order to remove contaminants. The polishing step, which is not likely to be part of the processing for a commercial implant, was introduced in order to facilitate the study of the impact of etching on surface integrity, phase transformation and strength. It was assumed that the effects of etching on a machined and annealed surface or on a sintered surface would be comparable. Samples were divided into different groups according to the treatment they received as reported in Table 1 (ten samples per group).

2.2. Chemical etching

Etching was carried out in HF 40% (Hydrofluoric Acid 40% QP Panreac, Spain) and followed by ultrasonic cleaning in DI water. The volume of acid was 1 mL by sample. Etching times between zero and two hours and a concentration of 40% were used rather than longer times and more diluted solutions because these conditions were shown to be the most appropriate for a fast and uniform roughening [12].

2.3. Surface integrity

An estimation of the average thickness of the layer of material removed during etching was calculated using the following formula:

$$t = \frac{\rho}{S}\Delta m \tag{1}$$

where t is the estimated removed thickness, Δm is the mass loss due to etching, ρ is the theoretical density of 3Y-TZP ($\rho = 6.1\ \mathrm{g\,cm^{-3}}$) and S is the total sample external area.

The surface of etched samples was examined by Scanning Electron Microscopy (SEM) and the near-surface was observed on transversal sections milled with a Focused Ion Beam (FIB, Neon40, Carl Zeiss AG, Germany) in order to detect phase transformation and damage. Sample surfaces were protected with a thin platinum coating to flatten the surface and minimize ion-beam damage and curtain effect during milling. The final polishing of the cross-sections was performed at 500 pA.

2.4. Ageing

Hydrothermal degradation tests (which will also be referred to as "ageing") were performed in an autoclave, at 134 °C, 100% steam atmosphere at 0.2 MPa pressure during thirty hours. These conditions have been suggested to be equivalent to roughly sixty years in vivo for polished 3Y-TZP [15].

2.5. Monoclinic phase content

Three specimens of each group (Table 1) were analyzed by X-ray diffraction (XRD) with a Bruker AXS D8 diffractometer using Cu-Kα radiation to detect and quantify the tetragonal–monoclinic transformation. The monoclinic fraction was determined by using the relation proposed by Toraya et al. [16]:

$$V_m = 1.311\frac{I_m\left(\bar{1}11\right) + I_m(111)}{1.311\left[I_m\left(\bar{1}11\right) + I_m(111) + I_t(101)\right]} \tag{2}$$

where V_m is the monoclinic volume fraction, $I_m\left(\bar{1}11\right)$ and $I_m(111)$ are the intensities of the monoclinic peaks and $I_t(101)$ is the intensity of the tetragonal peak.

2.6. Biaxial flexural strength

The biaxial flexural strength of the samples from the different groups (Table 1) was assessed by ball on three balls testing. The specimens were tested in an Instron 8511 servohydraulic fatigue testing machine with cobalt-cemented tungsten carbide balls of 5.9 mm diameter and a loading rate of 200 N/s. The fracture strength was calculated by using a numerical approximation of the maximum tensile stress as proposed by Börger et al. [17]:

$$\sigma_{max} = f.\frac{F}{t^2} \tag{3}$$

where F is the applied load, t the sample thickness and f a dimensionless factor. Provided that $0.55 < \frac{R_a}{R} < 0.9$ and $0.05 < \frac{t}{R} < 0.6$, an approximation of f for a determined Poisson's ratio can be calculated with the following formula:

$$f = c_0 + \frac{\left(c_1 + c_2\frac{t}{R} + c_3\left(\frac{t}{R}\right)^2 + c_4\left(\frac{t}{R}\right)^3\right)}{1 + c_5\frac{t}{R}}\left(1 + c_6\frac{R_a}{R}\right) \tag{4}$$

where R is the radius of the disk, R_a the support radius ($R_a = 3.4$ mm) and c_i ($i = 0, \ldots 6$) tabulated constants which depend on the Poisson's ratio ν [17]. For 3Y-TZP, $\nu \approx 0.3$ [18], which leads to the following values: $c_0 = -17.346$, $c_1 = 20.774$, $c_2 = 622.62$, $c_3 = -76.879$, $c_4 = 50.383$, $c_5 = 33.736$, $c_6 = 0.0613$.

2.7. Fractography

The fractographic examination was a complicated task because samples were broken into tiny pieces. However for some of the specimens it was possible to identify the fracture origin by SEM.

2.8. Statistical analysis

Statistical analysis of the strength testing results was performed using SPSS® software (version 20, SPSS Inc., Chicago, IL, USA). A two-way ANOVA with a 5% significance level was used to evaluate the