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Hydrofluoric acid etching of dental zirconia. Part 1: etching mechanism and surface characterization

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ABSTRACT

Rough surfaces have been shown to promote osseointegration, which is one of the keys for a successful dental implantation. Among the diverse treatments proposed to roughen zirconia, hydrofluoric acid (HF) etching appears to be a good candidate, however little is known about this process. In this work, the effect of HF concentration and etching time on the surface topography and chemistry of yttria-stabilized zirconia was assessed. Besides, to understand the etching mechanism, the reaction products present in solution and on the surface were characterized. The results indicate suitable parameters for a fast and uniform roughening of zirconia. The formation of adhered fluoride precipitates on the surface is reported for the first time and highlights the importance of cleaning after etching. Finally, it is shown that monitoring the time allows controlling the surface roughness, smooth–rough transition and fractal dimension, which should make possible the fabrication of implants with an optimal topography.

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]. While monolithic zirconia has been almost abandoned for orthopedic applications, in the last decade its use in restorative dentistry has been growing fast [2]. 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 [3]. 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 [4,5].

The key to solve the problem of bone loss mentioned above is to achieve a good osseointegration, which depends on numerous parameters such as surface topography and chemistry [6]. In particular it has been shown that rough surfaces exhibit a better bone response than smooth ones, and that the combination of micro- and nano-scale roughness could have synergistic effects [7–9]. Nevertheless, what is the optimal roughness for a dental implant remains unclear [8,9]. On the other hand, a complementary approach to the classical roughness parameters calculation is to perform a fractal analysis. It has been demonstrated that osteoblastic cells proliferation and adhesion is strongly correlated to fractal parameters [10]. There is therefore a strong interest in developing processes which allow controlling the roughness and the fractal dimension of a surface.

Among the different surface chemical treatments already experimented in the literature to achieve this purpose, hydrofluoric acid (HF) etching appears to be a good candidate. Although other chemicals, such as hypophosphorous acid or an equimolar mixture of potassium hydroxide and sodium hydroxide, have been reported to successfully etch Y-TZP [11,12], HF presents the advantage to be a fast etchant at room temperature. More importantly, Gahlert et al. evidenced that HF etching of zirconia implants enhances

Abbreviations: AFM, atomic force microscopy; DI water, deionized water; EDS, energy dispersive spectrometry; ESI-FTMS, electrospray ionization Fourier transform mass spectrometry; HF, hydrofluoric acid; SEM, scanning electron microscopy; SRC, smooth–rough crossover; TEM, Transmission electron microscopy; WLI, white light interferometry; XPS, X-ray photoelectron spectroscopy; Y-TZP, Yttria-stabilized tetragonal zirconia polycrystals; 3Y-TZP, 3 mol% Y-TZP.

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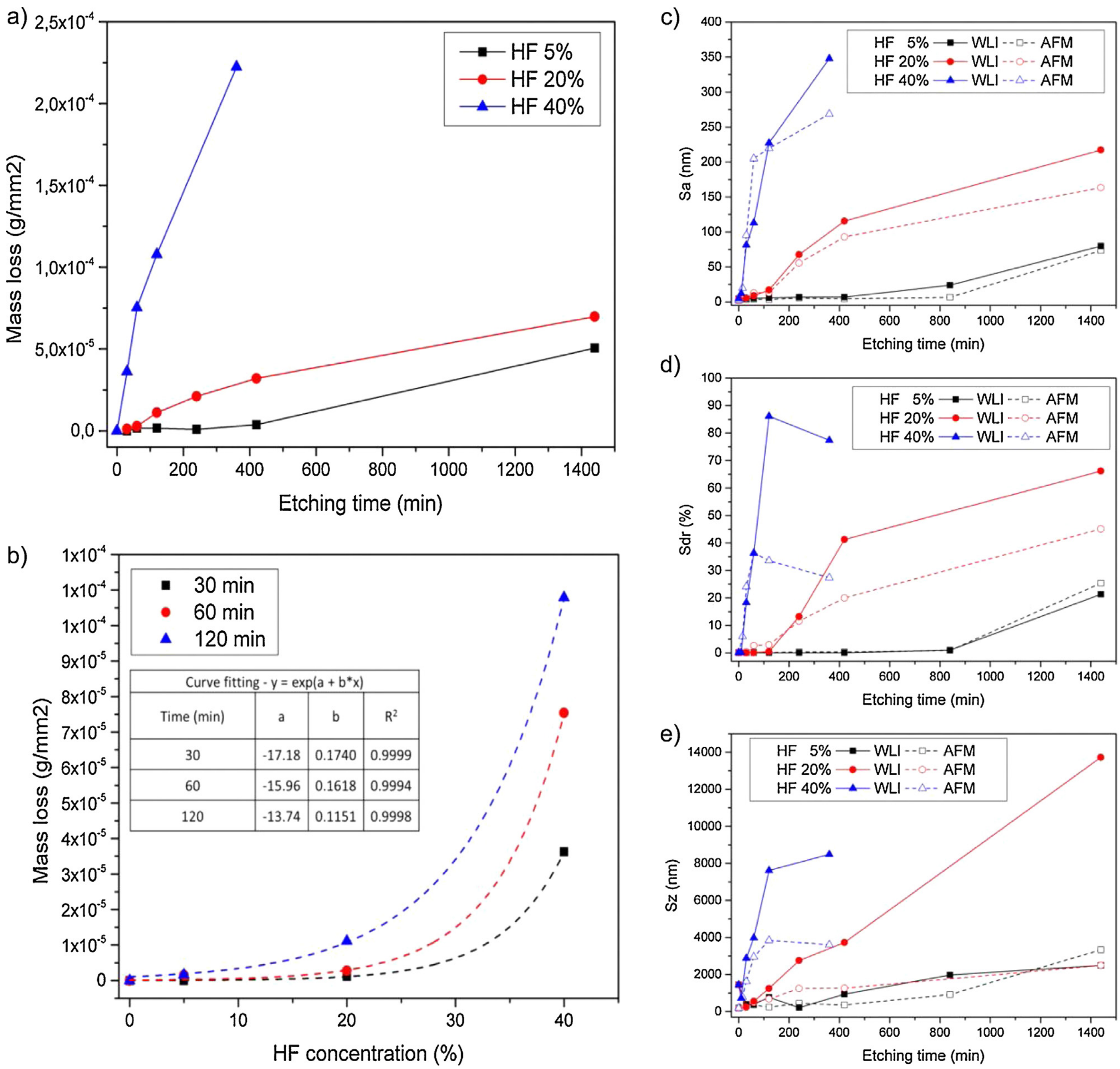

Fig. 1. Left: mass loss per initial sample external area as a function of (a) etching time for different HF concentrations, (b) HF concentration for different etching times. Right: (c) Sa, (d) Sdr and (e) Sz parameters determined from AFM and WLI data as a function of etching time for different HF concentrations. For all graphs each data point corresponds to a distinct specimen.

bone apposition resulting in high removal torque values [13]. Besides, HF etching can be successfully associated to sandblasting. Ito et al. showed that the combination of both treatments leads to an increase in the proliferation rate and expression of ALP activity of osteoblast-like cells (MC3T3-E1) [14] and Bergemann et al. found recently that it enhanced the human primary osteoblast maturation [15]. Additionally, the incorporation of fluoride at the surface could enhance osteoblastic differentiation and interfacial bone formation, as it does for titanium [16]. Finally, zirconia dental implants with acid etched surface are already commercialized (CeraRoot implants with ICE^{TM} surface) and apparently have shown a similar or higher success rate as compared to titanium implants after five years of follow-up [17].

Despite of numerous studies in which HF has been used for the etching of Y-TZP, to the best of the knowledge of the authors, very little is known about the chemical reaction involved. Besides, the influence of parameters such as time and concentration is not documented. The objectives of the present work are therefore to determine suitable conditions for a fast and uniform roughening of dental zirconia, to provide a complete surface characterization with a special emphasis on topography and to contribute to the understanding of the etching mechanism. Questions related to the influence of etching on the mechanical properties and long-term reliability are treated in a second article [18].

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), as described in previous work [19]. The sin-