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Research Paper

Surface roughened zirconia: towards hydrothermal stability

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ABSTRACT

Surface roughness is needed in several yttria-stabilized zirconia components used in restorative dentistry for osseointegration or adhesion purposes. This can be achieved by different treatments, which may also modify the microstructure of the surface. Among them, sandblasting and chemical etching are widely used, but their effect on hydrothermal aging of zirconia is not fully understood. In the present work, the zirconia long-term stability of rough surfaces prepared by these techniques is analyzed and a method is proposed for preventing hydrothermal aging while maintaining the original surface appearance and mechanical properties. The method involves pressure infiltration of a Cerium salt solution on the roughened surfaces followed by a thermal treatment. The solution, trapped by surface defects and small pores, is decomposed during thermal treatment into Cerium oxide, which is diffused at high temperature, obtaining Ce co-doping in the near-surface region. In addition, the microstructural changes induced in the near-surface by sandblasting or chemical etching are removed by the thermal treatment together with surface defects. No color modification was observed and the final roughness parameters were in the range of existing implants of proved good osseointegration. The aging resistance of Ce co-doped materials was strongly enhanced, showing the absence of aging after artificial degradation, increasing in this way the surface mechanical integrity.

The proposed treatment is easily applicable to the current manufacturing procedures of zirconia dental posts, abutments, crowns and dentures, representing a solution to hydrothermal aging in these and other biomedical applications.

1. Introduction

In the last decade, yttria-stabilized zirconia ceramics have been progressively occupying a more relevant role in restorative dentistry, thanks to their superior strength, moderate fracture toughness and biocompatibility (Denry and Kelly, 2008). These mechanical properties are associated to the sub-micrometric grain size and to the transformation toughening mechanism.

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The tetragonal phase, retained at room temperature in a metastable state thanks to the presence of 3 mol% of Yttrium oxide, can transform into the stable monoclinic phase under the local tensile stress at the tip of a crack under loading. The transformation is accompanied by an increase in volume of about 4.5%, and since it is constrained by the surrounding elastic material, compressive stresses are induced, which enhance the crack propagation resistance (transformation toughening) (Garvie et al., 1975). The good combination of fracture toughness and strength of 3Y-TZP allows its employment in a series of applications, which include dental crowns, dental implants, abutments, orthodontic brackets and fixed partial dentures (FPD's) (Conrad et al., 2007; Denry and Kelly, 2008; Kelly and Denry, 2008).

The main limitation of zirconia is represented by low temperature degradation (LTD), also known as hydrothermal degradation or aging. It consists in the spontaneous transformation of the surface to the monoclinic phase in humid environments and moderate temperatures, including human body conditions (Chevalier et al., 2007). LTD is slow at room temperature and interests only a superficial layer of few micrometers in well-densified 3Y-TZP, but it is accompanied by the formation of surface microcracks, surface roughening and loss of cohesion, making the material unsuitable for orthopedic joint replacement where surface stability is fundamental.

Sandblasting is a treatment that is commonly applied in the manufacturing of zirconia dental crowns in order to increase the surface area and roughness. This, in turn, promotes the adhesion between the crown and either the luting cement or the veneering porcelain, by increasing wettability, surface energy and the bonding area (Fischer et al., 2008; Kern and Wegner, 1998; Wolfart et al., 2007).

Roughness is created through an erosive wear process in which high-speed hard particles impact on the surface and chunks of material are removed. During the impact, local surface plastic deformation and subsurface cracks may be generated. Lateral cracks, parallel to the surface, contribute to the erosion process, whereas radial cracks, perpendicular to the surface, may impair the material performance (Lawn, 1993).

During mechanical modification of the surface by sandblasting, local phase transformation may take place, which may induce damage as well as compressive forces as a result of the local volume increase associated with the transformation. The sole sandblasting may increase or decrease the strength depending on the trade-off between the effect of the surface compressive layer resulting from the process and the characteristics of the additional surface defects introduced (Chintapalli et al., 2014; Kosmač, 2008). It is important to underline that the compressive stresses disappear if a heat treatment is performed after sandblasting, as it happens during the veneering process, due to reconversion of the monoclinic layer and stress release. As a result, the superficial cracks are exposed to tensile stresses, lowering the strength. It was shown that the optimization of sandblasting parameters allows generating lower damage during the process, limiting the strength decrease associated to the thermal treatment (Chintapalli et al., 2014).

Sandblasting delays the beginning and lowers the kinetics of LTD. Since the aging behavior of zirconia of sandblasted plus annealed specimens is similar to sintered plus polished specimens, the lower LTD in the sandblasted state must be related to the superficial compressive layer and the local plastic deformation generated. (Chintapalli, 2012; Kim et al., 2010; Kosmač, 2008). Nevertheless, specimens obtained maximizing the strength by choosing optimum sandblasting conditions, may suffer a drop in strength after artificial degradation, being the drop severe after long and aggressive aging treatments (Chintapalli, 2012; Kosmač, 2008; Papanagiotou et al., 2006).

Chemical etching has been reported to be an efficient technique to produce a fine roughness on zirconia, down to the nanoscale (Hempel et al., 2010). Gahlert et al. (2010) evidenced that hydrofluoric acid (HF) etching of zirconia implants enhances bone apposition resulting in high removal torque values. Other chemicals, such as hypophosphorous acid or an equimolar mixture of potassium hydroxide and sodium hydroxide, have been reported to successfully etch Y-TZP (Casucci et al., 2010; Gruber et al., 2012). However, HF presents the advantage to be a fast etchant at room temperature.

In recent studies, it was shown that by introducing surface roughness in 3Y-TZP, the cell response was similar to titanium and alumina, concluding that roughened zirconia surface represents an appropriate substrate for proliferation and spreading of osteoblastic cells (Bächle et al., 2007; Wenz et al., 2008; Yamashita et al., 2009). It was also reported that zirconia dental implants with acid etched surface (CeraRoot implants with ICE™ surface) showed a similar or higher success rate as for Titanium implants after 5 years of follow-up study (Oliva et al., 2010).

Besides, Cooper et al. (2006) found that the incorporation of fluoride at the surface of titanium implants could enhance osteoblastic differentiation and interfacial bone formation. More recently, Ito et al. (2013) showed that the combination of sandblasting with HF etching leads to an increase in the proliferation rate and expression of ALP activity of osteoblast-like cells (MC3T3-E1).

The stability of 3Y-TZP surface is fundamental for the performance in dental applications, since the surface is responsible for transferring the load from the veneer/luting cement to the crown/abutment or from the implant to the bone. Although water may be not directly in contact with zirconia dental crowns, it can penetrate into luting cements and have access to the material surface, which can be therefore exposed to degradation (Jevnikar et al., 2000). Therefore, hydrothermal degradation may play a role on the stability of the crown surface and finally on the life time of the part. The same situation is found in implants connected to the bone, where body fluids are always present and the role of the surface is of extreme importance. Therefore, there is a clear need for improving 3Y-TZP aging resistance and guarantee its surface stability.

Several works have proved that co-doping Y-TZP with Ce can improve substantially the degradation behavior (Boutz et al., 1995; Lin and Duh, 2003; Marro et al., 2011; Sato et al., 1987), probably due to the reduction in concentration of oxygen vacancies decreasing in this way the diffusion of water species which has been recognized as the trigger mechanism for the degradation phenomenon (Guo, 1998). In a recent work by the authors (Camposilvan et al., 2015), Ce co-doping was performed by infiltration in the pre-sintered state to increase the degradation resistance of 3Y-TZP. The process consists in the infiltration of porous pre-sintered 3Y-TZP