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Micropillar compression inside zirconia degraded layer

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Abstract

In the dental field, Yttria-doped Tetragonal Polycrystalline Zirconia (Y-TZP) plays an important role due to its high mechanical properties, good aesthetics and bio-inert behavior. Surface mechanical properties are crucial for Y-TZP especially when it comes to osseointegration or contact loading, since it may undergo a spontaneous aging phenomenon when exposed to humid environment, creating a thin degraded layer that affects surface integrity. In this work, polished samples of Y-TZP have been artificially aged, and micropillars with diameters in the range 3.3–0.3 μm have been milled by FIB inside the degraded layer and in the reference non-aged surface. Reproducible stress–strain curves were obtained by testing the micropillars in compression, demonstrating that this technique is suitable for assessing the degraded surface properties. Mechanical and failure behavior are significantly different for the degraded micropillars due to the presence of microcracks, while important differences are observed when reducing the micropillar diameter.

Keywords: Zirconia; Micropillar compression; Low temperature degradation; Small-scale testing

1. Introduction

Structural zirconia ceramics are widely and increasingly used in dentistry due to their outstanding properties, especially in terms of fracture toughness (K_{Ic}), biocompatibility and aesthetics [1]. The main mechanism responsible for the relative high value of K_{Ic} is transformation toughening, that is, the transformation of the metastable tetragonal (*t*) phase into monoclinic phase (*m*) in front of the crack tip triggered by the high local stress generated under loading. During this transformation, a local volume expansion of approximately 4.5% takes place, inducing a compressive component at the crack tip that hinders its propagation. The result is a net increase in K_{Ic}, which depends on different variables related to the particular alloying system and microstructure of zirconia [2].

Here the attention is addressed to yttria-stabilized tetragonal polycrystalline zirconia (3Y-TZP), a system with very fine microstructure composed almost entirely of tetragonal grains with size of approximately 350 nm. The 3 mol% yttria content is the result of optimization in order to attain high mechanical strength. Approximately 1200 MPa flexure strength is measured for a standard processed material, which is the highest among single-phase ceramics, and a considerable K_{Ic} of ∼4.5 MPa $\sqrt{\text{m}}$.

At present, 3Y-TZP is being extensively used in dentistry for the production of dental crowns, bridges, abutments, dentures and dental implants [3]. The microstructure, topography, and mechanical properties of the surface are of extreme importance for all these applications, especially when it comes to load transfer by contact loading. In this sense, the long-term surface stability of zirconia became an issue after the discovery that hydrothermal degradation, an aging phenomenon that affects the surface of zirconia when exposed to humid environment and temperatures around 250 °C, may also take place at much lower temperatures including that of the human body. During aging, due to the diffusion of water species, the tetragonal–monoclinic (*t*–*m*) transformation starts to occur spontaneously on the surface through a nucleation-and-growth mechanism. After long exposure, grain boundary microcracks are formed within a thin

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superficial layer and monoclinic uplifts appear on the surface producing an increase in roughness [4]. The process is also accompanied by grain pull-out, a considerable decrease in surface hardness that can be measured by nanoindentation and the deterioration of scratch resistance [5–7]. The extent of transformation can be observed, and eventually measured, in terms of fraction of monoclinic phase content from its first appearance on some isolated grains [8] to the progression through the first superficial layers [9] and into the volume [10].

Even though all these aspects have been widely documented by accelerated aging tests in water vapor at the standard sterilization temperature and pressure, there is still lack of knowledge on how mechanical properties are modified inside the transformed layer, which is generally few μm in thickness after long exposure to the human body environment. It was observed by TEM that degradation microcracks develop anisotropically, being mainly orientated along planes roughly parallel to the free surface [11]. The spatial distribution of microcracks in the degraded volume was also measured by means of focused ion beam (FIB) tomography [12], confirming the anisotropic distribution.

Small-scale testing refers to mechanical tests performed on a reduced volume of material, an approach that can shed some light on the mechanical behavior of the degraded surface of zirconia. A first and well-known example of these techniques is represented by nanoindentation, which finds its limitation in the complex stress state surrounding the indenter tip. With the development of FIB and other high precision shaping techniques, coupled with the load–displacement resolution offered by the technology of nanoindenters, new methods started to appear. By milling small volume samples with suitable geometry, the response of materials to compression, bending, torsion and tension states could be probed. For more details about these techniques, see Legros et al. [13]. In metallic monocrystals, the main result of these studies is that the rule "the smaller being stronger" holds for many systems and models related to strain gradients and interaction of dislocations with free surfaces have been developed for explaining this particular behavior [14,15].

In the case of ceramic monocrystals, only few authors have used micropillar compression testing, often with the main objective of observing the existence of a brittle–ductile transition. In effect, a ductile behavior could be observed by reducing the sample size below some critical value that lies roughly between tens and hundreds of nanometers. Several materials conventionally known as "brittle" have shown plasticity features at the small scale: Si [16], GaAs [17], MgO [18] Al_2O_3 [19] and SiC [20]. At the same time, superelastic and shape-memory effects were recently observed by Lai et al. [21] during compression of tetragonal zirconia micropillars highly doped with Y and Ce. Size-dependent phenomena related to flow stress in ceramic micropillars have also been documented by Korte and Clegg [18], showing a similar behavior to metals once dislocations are activated by high stresses. Recently, the flexural response of polycrystalline micro-cantilevers milled by FIB inside the zirconia degraded layer has been studied by Camposilvan et al. [22], observing a significantly different behavior depending on the direction of the applied stress, thus confirming that the anisotropic damage affects the mechanical properties inside the layer.

In the present work, micropillar compression testing is applied to 3Y-TZP. Polycrystalline micropillars are milled by FIB from the surface of fully degraded and non-degraded zirconia, with the main objective of studying the effect of degradation on the mechanical behavior.

2. Experimental

Commercial spray-dried zirconia powder (TZ-3YSB-E, Tosoh Corp.) was pressed isostatically at 200 MPa in a rod shape and sintered at 1450 °C in air inside a tubular furnace for 2 h, obtaining a ceramic with density of 6.06 ± 0.02 g/cm^3 ($99.5 \pm 0.3\%$ of the theoretical value) as measured by the Archimedes' method. The rod was cut into disks of. ~1.5 mm thickness and these were ground and polished with diamond pastes down to less than 20 nm Ra. Few samples were exposed to artificial degradation in autoclave, under steam atmosphere at 134 °C and 2 bar pressure, for 145 h. The grain size was measured by the linear intercept method on polished and thermally etched (1300 °C) surfaces.

X-ray diffraction (XRD) patterns were collected before and after artificial degradation using a Bruker D8 Advance diffractometer with Cu *K*-α radiation and $\theta/2\theta$ configuration in the region 25–35°. The intensity of selected peaks was used to calculate the monoclinic volume fraction by applying the equation of Toraya et al. [23]. Hardness and indentation fracture (IF) toughness were measured by the Vickers indentation method with a load of 10 kg. The IF toughness was calculated with the formula proposed by Niihara et al. [24]. Nano-hardness and elastic modulus were measured with a Berkovich indenter mounted on a MTS Nanoindenter XP equipped with a continuous stiffness measurement (CSM) module. 4 matrices of 3×3 nanoindentations were performed at random locations on the disks surface, with constant deformation speed of 0.05 s^{-1} to a penetration depth of 500 nm, which was selected to get stable measurements within the superficial layer.

The degradation time was chosen in order to produce a superficial fully degraded layer with a thickness greater than 13 μm [10]. In this way, micro-sized fully degraded samples could be obtained from the surface. For doing so, both degraded and reference disks were cut along the diameter and the cross-section was polished using diamond films on a tripod fixture (Struers A/S). The disk halves were mounted on inclinable holders for scanning electron microscopy (SEM) using high strength silver adhesive and coated with a few nanometers Au/Pd layer to increase conductivity and avoid charging phenomena during milling.

The holders were introduced in a Zeiss Neon 40 dual beam microscope in order to mill by FIB micropillars with aspect ratio between 2:1 and 4:1 from the surface area adjacent to the cross-section edge. A major issue in this procedure is represented by the taper angle that forms when employing FIB to mill cross-sectional surfaces. A way to limit this effect is by milling the final shape with multiple steps, so that the last current can be small enough to allow careful focusing and stigmation. At the