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ScienceDirect

Acta Materialia 80 (2014) 239–249

Acta MATERIALIA

www.elsevier.com/locate/actamat

Small-scale mechanical behavior of zirconia

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Received 9 April 2014; received in revised form 17 July 2014; accepted 20 July 2014

Abstract

The surface stability of yttria-doped tetragonal polycrystalline zirconia is critical for load-bearing biomedical applications. In this work, the small-scale mechanical behavior of this material is probed by employing the in situ micro-cantilever bending technique to near-surface regions. Micro-cantilevers are milled by the focused ion beam technique in the as-sintered condition as well as after hydrothermal degradation by water vapor and tested in order to investigate the effect of degradation on the local flexural response. Results demonstrate that the technique is reliable for assessing the mechanical properties of thin superficial layers and their dependence on orientation. In the non-degraded material, the flexural strength is surprisingly higher than in standard-size specimens and transformation-induced plasticity takes place during testing, inducing defects that become critical at the failure stress. The strength and stiffness of cantilevers obtained from the degraded surface are indeed much lower, and the magnitude of the effect clearly depends on their orientation with respect to the surface. These results are discussed in terms of the presence and spatial distribution of microcracks nucleated during hydrothermal degradation.

Keywords: Zirconia; Small-scale testing; Hydrothermal degradation; Transformation-induced plasticity; Micro-cantilever

1. Introduction

Knowledge about the mechanical behavior of materials has increased noticeably since the development and implementation of small-scale testing. The new capabilities offered by these techniques have given us the opportunity to understand deformation, strengthening and failure at the micro/nanoscale, and to relate such properties to the behavior at the macroscopic scale. Unlike soft metallic monocrystals, this approach has been barely attempted in ceramic materials, with the main exception of silicon. Nevertheless, small-scale testing in ceramics can offer important information when applied to thin films, tiny devices or microstructural constituents, for which substantial size effects can exist. Here, attention is addressed to the study of the mechanical properties of the surface layer of zirconia degraded by hydrothermal exposure, since its stability is fundamental for its long-term success as a biomaterial.

Zirconia is one of the most employed technical oxide ceramics, especially when partially stabilized with a suitable amount of yttrium oxide. Tetragonal zirconia polycrystals with 3 mol.% of yttria (3Y-TZPs) have a metastable tetragonal structure at room temperature and exhibit very high tensile strength thanks mostly to their sub-micron grain size and moderate fracture toughness. The main mechanism of toughening is associated with the stress-induced martensitic transformation from tetragonal (t) to monoclinic (m), which is accompanied by ∼4.5% volume expansion. When the *t-m* transformation is triggered by the high tensile stress in front of a crack tip, the resulting volume change is constrained by the surrounding

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http://dx.doi.org/10.1016/j.actamat.2014.07.053
1359-6454/

material and hence lowers the crack driving force by inducing a compressive component on its flanks [1]. Thanks to these properties, zirconia-based ceramics have been extensively used as load-bearing materials for different biomedical applications such as for dental restorations and joint replacements.

The metastability responsible for transformation toughening is also responsible for the so-called low-temperature degradation (LTD), hydrothermal degradation or simply aging: when 3Y-TZP is exposed to a humid environment at moderate temperatures, the surface starts to transform spontaneously into the stable phase. The transformation is triggered by water species, which act as catalysts for the martensitic structural change [2]. Islands of monoclinic phase are first formed at the surface near grain junctions [3] or cubic grains, which may be present as a secondary phase [4]. The volume expansion is accommodated by surface uplifts that grow in size with further exposure, producing superficial roughening [5]. Once the surface grains are transformed, the transformation of the adjacent grains below the surface is assisted by the tensile stresses that compensate the compressive stress state produced by the volume expansion on the surface. Nevertheless, the progression of the transformation is far from being instantaneous because it is controlled by the diffusion of water species. Additionally, the martensitic transformation is accompanied by grain decohesion and microcracking, leading in some cases to grain pull-out. Aging is therefore an autocatalytic phenomenon which starts from the surface and affects only a very limited depth in the micrometer range, at the temperatures at which 3Y-TZP is employed as a biomaterial [6].

The transformation that occurs during LTD has been widely studied by using different techniques, such as X-ray diffraction or micro-Raman spectroscopy, to detect the presence of the monoclinic phase [7,8]. The early stages of the transformation can be detected by atomic force microscopy or optical interferometry, thanks to the surface roughness produced by uplifts formation. A cross-section of the surface also reveals the degraded layer due to the granular appearance induced by grain pull-out during polishing [9]. All these techniques are used to detect LTD either on explanted prosthesis or on artificially degraded samples exposed to water vapor and pressure, normally under typical sterilization conditions of 134 °C and 2 bar, as suggested in the ISO standard 13356. With the aid of artificial LTD, the degradation phenomenon has been well characterized and the parameters having a stronger influence on aging, such as time, temperature, humidity, grain size and residual stresses, have been elucidated [10,11]. Recently, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) observations of focused ion beam (FIB) milled micrometric size cross-sections of the degraded layer, have also allowed the microstructural changes and damage induced by LTD to be studied in detail [12]. The results of this study showed that subsurface microcracking is essentially anisotropic, being the cracks preferentially oriented along planes parallel to the exposed surface.

LTD raised many concerns regarding the employment of zirconia as a load-bearing biomaterial in view of its phase stability and effect on strength and reliability after long term exposure to corporal fluids. Actually, the flexural strength of 3Y-TZP bulk specimens with 0.32 μm grain size does not change, even after the exposure to 30 h of artificial aging [13], which may be compared to an average human life, since 1 h of this treatment is equivalent to roughly 3–4 years under human body conditions (it is important to emphasize that the above equivalence holds for stress-free specimens and does not account for different factors like stress state in vivo) [14]. Nevertheless, in many load-bearing applications, the surface reliability of 3Y-TZP does play a critical role since it is responsible for transferring the load from the implant to the body or between the two sliding parts of a joint. Unfortunately, the surface mechanical properties of 3Y-TZP are strongly affected after degradation, as demonstrated by the decrease in surface hardness, elastic modulus and scratch resistance reported by different authors [10,11,15]. However, the strength of the degraded layer has never been directly measured. An attempt to do so was made in a porous 3Y-TZP by means of bending tests [16]. The aim of the present paper is to measure directly the strength of the degraded layer induced in fully dense 3Y-TZP with the aid of small-scale testing.

With the combination of FIB milling and nanoindenter testing capabilities, traditional mechanical tests have been reproduced in the last years employing samples with a size in the micrometer range, measuring directly the properties of reduced volumes. The first and most successful of these new techniques is represented by micro-pillar compression, where a micro-pillar is first ion-milled on the material surface (or obtained with other techniques) and then tested in compression using a nanoindenter with a flat-punch tip [17]. This technique allowed the observation of size effects in metals and ceramics by measuring the stress–strain response of individual slip systems in monocrystals [18]. Other small-scale techniques have also been applied to evaluate the micro-mechanical behavior under different stress states, such as bending and under a pure tensile stress. For more detailed information, see Legros et al. [19].

In the present work, micrometric cantilevers are milled with FIB on the surface of degraded and as-sintered 3Y-TZP and tested in flexure, in order to obtain reliable strength values and reproducible stress–strain curves. The dependence of the mechanical response of degraded specimens on the orientation is assessed by testing cantilevers milled with their main axis either parallel or perpendicular to the degraded surface. In this way, the effect of the damage anisotropy observed in the degraded layer is studied.

2. Experimental

3Y-TZP spray-dried powder produced by TOSOH Corp. under the designation TZ-3YSB-E was pressed isostatically at 200 MPa for 10 min, to obtain a rod-shaped