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Annealing aged zirconia: Study of surface mechanical properties at the micrometric length scale

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Abstract

The annealing of hydrothermal aged zirconia has been studied by analysing the changes in microstructure and surface mechanical properties in terms of the annealing temperature. In this experimental work, a systematic micro- and nanomechanical study has been conducted in 3 mol% yttria-stabilized tetragonal polycrystalline zirconia (3Y-TZP) aged at 134 °C for 60 h and annealed at 600 °C and 850 °C for 1 h. Advance characterization techniques (micro-Raman, field emission scanning electron microscopy and focused ion beam) have been used to study the near surface microstructural changes induced by these treatments. The mechanical properties and resistance to damage of the near surface are determined by means of nanoindentation and nanoscratch testing. The observed behaviour is discussed in terms of the change in microstructure induced after ageing and annealing.

Keywords: 3Y-TZP; Monoclinic to tetragonal phase transformation; Annealing treatment; Indentation hardness and indentation elastic modulus; Scratch resistance

1. Introduction

Zirconia ceramic materials are widely and increasingly used in dentistry due to their outstanding biocompatibility and aesthetics.[1] One of these materials that has received increasing attention in recent years is 3 mol% yttria-stabilized tetragonal polycrystalline zirconia (3Y-TZP), which is widely used to fabricate multiunit fixed partial dentures,[2,3] inlays[2,4,5] and implants,[6] due to its excellent mechanical, thermal, and tribological properties, biocompatibility and corrosion resistance.[7]

However, with the presence of water, 3Y-TZP undergoes a spontaneous unfavourable phase transformation from tetragonal to monoclinic *t-m* at relatively low temperatures.[8,9] The phase transformation starts at the surface and progresses as a surface transformed layer that grows very slowly in thickness.[10] The transformation strain (~8% shear strain and 4–5% volume increase) produces surface roughening,[11] grain pull out, macro- or even microcracks and loss of surface mechanical properties. This phenomenon is referred to as hydrothermal ageing or low temperature degradation (LTD), and it may be very detrimental for those biomedical implants whose surface integrity is of paramount importance for their functionality.[12] Both, *t-m* transformation and microcracking, are confined into a surface layer with a thickness that depends on the composition, porosity, grain size, temperature of ageing, time and pressure.[13]

In this paper we address the question of whether the mechanical properties of 3Y-TZP can be recovered by annealing after ageing. It is well known that the *t-m* transformation can be fully reversed by suitable annealing, but there is a lack of information on whether the mechanical properties of the degraded surface layer are also fully recovered at relatively low annealing temperatures. Since intergranular microcracks are induced during ageing, the objective of the present work is to clarify if annealing is able to rebuild microcracked grain boundaries with the same original strength. Therefore, the present study aims to evaluate

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the effect of phase transformation and microcracking into the surface in terms of mechanical and tribological properties at micro- and nanometric length scale.

2. Experimental procedure

2.1. Sample preparation

Specimens were processed from zirconia powder stabilized with 3 mol % yttria (TZ-3YSB-E, Tosoh, Tokyo, Japan). The green body was obtained through cold isostatic pressing at 200 MPa, forming rods 10 mm in diameter. The material was sintered for 2 h at 1450 °C, with heating and cooling rate of 3 °C min^{-1}. The rods were cut in disks 2 mm thick. After sintering, the samples were characterized with respect to their final density, grain size and crystalline phases present. For determining the density of the sintered samples, the Archimedes technique was used with distilled water as the buoyant medium, being 6.03 ± 0.01 g cm^{-3} for the tetragonal 3Y-TZP. Grain size for the as-sintered specimen was provided by analysis imaging using field emission scanning electron microscopy, resulting in a material with grain size 0.34 ± 0.02 μm. Further details on these materials and on the preparation of specimens can be found elsewhere.[14,15]

Prior to the low temperature degradation (LTD) test, the disc specimens were previously polished with SiC paper and diamond paste finishing with colloidal silica, in an ordinary metallographic polisher. The quality of the finishing was checked by confocal laser scanning microscopy in order to avoid the presence of scratches on the surfaces prior to testing. Finally, all specimens were cleaned ultrasonically with distilled water for 5 min and dried with a pure air.

Subsequently, specimens were degraded in an autoclave in the presence of water steam at 134 °C and 0.2 MPa pressure during 60 h (60H). These conditions are roughly equivalent to many years at human body temperature (more than a human lifetime).[16,17] The thickness of the degraded layer after 60 h reached values of approximately 10 μm. Also, disks of 60H were sectioned and carefully polished in order to measure the volume fraction of monoclinic phase and the elastic modulus at different depths below the surface.

The degraded specimens were thermally treated at 600 and 850 °C during 1 h in order to reverse the phase transformation created during the LTD process (from monoclinic to tetragonal phase, *m-t*). The codes used for the specimens tested in the present work are shown in Table 1.

Table 1
Codes for ageing and annealing treatments and phase composition.

Code	Description	$V_{monoclinic}$ (%)
AS	As-sintered	<3
60H	Ageing: 60 h, 134 °C, 0.2 MPa	86
60H+600 °C	As 60H + annealing (600 °C, 1 h)	40
60H+850 °C	As 60H + annealing (850 °C, 1 h)	<5

2.2. Structure characterization

Raman spectra were collected with a spectrometer Jobin-Yvon LabRam HR 800 coupled to an Olympus optical microscope BXFM with an objective of 100× and to a CCD detector cooled with liquid nitrogen. Raman spectra were recorded using the 532 nm laser wavelength excitation and an acquisition range from 100 up to 3000 cm^{-1}. The spectrum integration time was 60s, with averaging the recorded spectra over three successive measurements. The measurements for 60H were carried out not only on the surface of the disks, but also in the cross section at different depths. For the as-sintered (AS) and annealed specimens only three measurements were done on the surface. Finally, in order to estimate the monoclinic volume fraction for the different specimen conditions, the following expression was used:[18]

$$V_m = \frac{I_m^{181} + I_m^{190}}{0.32(I_t^{147} + I_t^{265}) + I_m^{181} + I_m^{190}} \quad (1)$$

where I_m and I_t represent the integrated intensities of the monoclinic and tetragonal peaks, respectively. The super-indexes identify the μ-Raman shift in cm^{-1}. For all spectra, a linear subtraction of the background was made and, the integrated intensity bands were calculated by fitting Lorentzian distribution functions.

2.3. Mechanical response

The mechanical characterization at micro- and nanometric length scale included the evaluation of the effective hardness (H) and elastic modulus (E) through a nanoindenter XP apparatus from MTS. It was equipped with a continuous stiffness measurements (CSM) modulus, allowing a dynamic determination of the mechanical properties during indentation.[19] Indentations were organized in a regularly spaced array of 16 imprints (4 by 4) and 2000 nm of maximum displacement into the surface (or until reaching the maximum applied load, i.e. 650 mN), and the results were averaged in order to have statistical signification. The distance between imprints were kept constant to 50 μm in order to avoid any overlapping effect. The strain rate was held constant at 005 s^{-1}. The indenter shape was carefully calibrated for true penetration depths as small as 60 nm by indenting a standard specimen of fused silica of accurately known Young's modulus (72 GPa). The values of hardness and elastic modulus were directly calculated using the Oliver and Pharr analysis.[19,20] The elastic modulus was also determined by indenting the section of the discs at depths intervals of 2 μm with a maximum displacement into the surface of 2000 nm. For each position at least three measurements were done.

Sliding contact tests at nanometer length scale were carried out by means of a nanoscratch fixture attached to the nanoindenter system refereed above. A Berkovich indenter was employed to scratch the different sets of specimens under constant loads of 50 mN and 100 mN and at a velocity of 10 μm/s over a length of 200 μm. Two different scans were done in each specimen.