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ScienceDirect

Acta Materialia 92 (2015) 290–298

Acta MATERIALIA

www.elsevier.com/locate/actamat

Lifetime estimation of zirconia ceramics by linear ageing kinetics

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Received 21 November 2014; revised 26 March 2015; accepted 1 April 2015

Available online 22 April 2015

Abstract—Up to now, the ageing kinetics of zirconia ceramics were mainly derived from the sigmoidal evolution of the surface phase transformation as a function of time, as quantified by means of X-ray diffraction (XRD). However, the transformation propagation into the material should be better to monitor the ageing kinetics. In this work, μ-Raman spectroscopy was used to quantitatively measure the transformation profiles in depth as a function of ageing time at 160 °C, 140 °C, 134 °C and 110 °C.

A linear relationship between the transformed depth and the ageing time was observed for all investigated yttria stabilized tetragonal zirconia polycrystals (3Y-TZP). Furthermore, the μ-Raman investigation of residual stresses in the subsurface of aged 3Y-TZPs showed that the highest tensile stress was located just ahead of the transformation front, indicating the key responsibility of stress accumulation for transformation front propagating into the material. Moreover, the linear kinetics of the transformation propagation were more accurate to calculate the apparent activation energy of the ageing process and allowed a more straightforward estimation of the lifetime of 3Y-TZP at body temperature, as compared to the conventional ageing kinetic parameters obtained from the surface transformation analysis by XRD.

Keywords: Zirconia; Linear ageing kinetics; Transformation propagation; μ-Raman spectroscopy

1. Introduction

The metastability of tetragonal zirconia benefits the fracture toughness and strength of yttria stabilized tetragonal zirconia polycrystals (Y-TZP), but could limit its longevity for biomedical applications. At the crack tip in a Y-TZP ceramic, tetragonal zirconia can transform to monoclinic phase, resulting in a local volume expansion and concomitantly inducing compressive stress that counteracts crack propagation. Therefore, the flexural strength and toughness of Y-TZP ceramics can be strongly enhanced by this transformation toughening effect [1,2]. In the presence of water or humidity however, the transformation from tetragonal to monoclinic (*t*-*m*) zirconia can occur spontaneously, even at room temperature (low temperature degradation or hydrothermal ageing) [1,3]. This can lead to increased wear rates with the release of small zirconia particles in the surrounding environment, aesthetic deterioration, reduced mechanical properties and even catastrophic failure [1,4–6]. Consequently, the life-time of Y-TZP based ceramics is significantly limited by the possible ageing problem. Therefore, the ageing kinetics of biomedical grade Y-TZP containing ceramics has to be carefully assessed for a safe biomedical application [7].

The ageing kinetics of Y-TZP ceramics are temperature dependent [8]. Since the hydrothermal ageing rate of Y-TZP ceramics at body temperature (37 °C) is very slow, requiring years to have a significant effect, *in vivo* investigation is obviously not practical. Therefore, hydrothermal treatments at intermediate temperatures (100–300 °C) in steam are normally used to accelerate the ageing rate of Y-TZP ceramics, allowing extrapolation of the ageing kinetics at body temperature from an Arrhenius plot [5,8].

Up to now, most ageing kinetic parameter studies were based on surface *t*- to *m*-ZrO_2 phase transformation profiles measured by X-ray diffraction (XRD) and fitted according to the Mehl–Avrami–Johnson (MAJ) model [9–14]. Based on this method, the apparent ageing activation energy of 3Y-TZP was calculated to be about 106 kJ/mol [9]. This also formed the basis for the commonly used statement: "1 h of autoclave treatment in steam at 134 °C is theoretically the same as 3–4 years *in vivo* at 37 °C" [15].

However, more and more research points out the importance of the transformation propagation [16–18], and the transformed depth should be better suited for monitoring the kinetics. Furthermore, there is an ongoing debate on whether the transformation process propagates linearly or nonlinearly. Linear ageing kinetics were reported when monitoring the transformation propagation [17,19,20], questioning the shape of the transformation front in the MAJ kinetic model [17]. Therefore, the ageing kinetics in

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http://dx.doi.org/10.1016/j.actamat.2015.04.001

1359-6462/

this work were interpreted by monitoring the transformation propagation.

Different methods can be used to quantify the depth of the transformed layer [17,19–21]. Recently, μ-Raman spectroscopy was used to quantify the m-ZrO_2 fraction profiles in depth [16,18,22–24], and it also allowed the measurement of residual stresses in zirconia ceramics [25–27]. The stress status in the subsurface of aged TZP ceramics, however, has never been reported.

Therefore, μ-Raman spectroscopy was used in this work to follow up the transformation propagation by quantifying the in-depth transformation profiles as a function of ageing temperature and time, and to assess the stress status at the transformation front. The resulting kinetic parameters were used to calculate the apparent activation energy and estimate the hydrothermal stability of a number of 3Y-TZP ceramics. The conventional method of following the surface phase transformation by XRD was performed as a reference to find out which method is most suitable to estimate the life-time of Y-TZP based ceramics at body temperature.

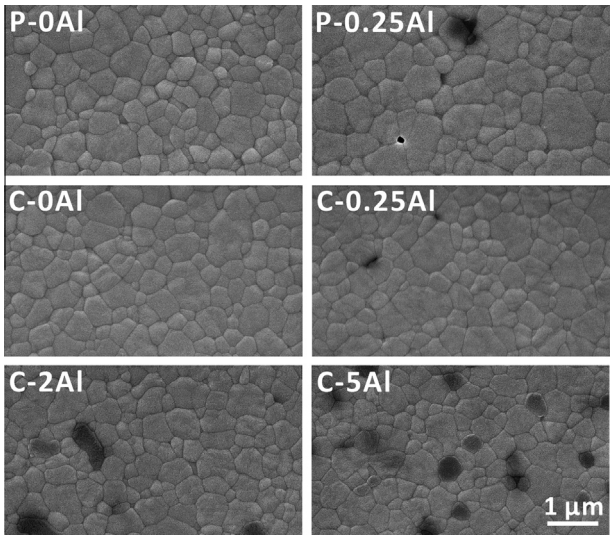

Fig. 1. SEM images of investigated 3Y-TZP ceramics (P-0Al, P-0.25Al, C-0Al, C-0.25Al, C-2Al and C-5Al).

2. Materials and methods

2.1. Experimental materials

In order to investigate the role of microstructural variations on the ageing kinetics, six different 3Y-TZP materials were studied. Two of them were prepared from yttria co-precipitated commercially available powder, i.e. TZ-3Y (Tosoh, Japan) and TZ-3Y-E (Tosoh, Japan, with 0.25 wt.% alumina), further named as P-0Al and P-0.25Al. The other four materials were prepared from yttria-coated zirconia powder, which allowed a combination of higher ageing resistance and higher fracture toughness [28]. The yttria-coated powder grades contain 0, 0.25, 2 or 5 wt.% alumina, and the resulting ceramics were named as C-0Al, C-0.25Al, C-2Al and C-5Al, respectively. More information on the preparation of the yttria-coated ZrO_2 ceramics is provided elsewhere [29].

The starting powders were cold isostatic pressed (CIP) at 200 MPa and pressureless sintered in air for 2 h at 1550 °C, yielding fully dense 3Y-TZP ceramics. X-ray diffraction (XRD) analysis revealed no evidence of monoclinic phase before ageing for all six 3Y-TZPs. The average grain size was measured to be 360 ± 165, 484 ± 225, 404 ± 198, 430 ± 205, 395 ± 204 and 384 ± 190 nm ($\pm$ is SD) from SEM images (Fig. 1) for P-0Al, P-0.25Al, C-0Al, C-0.25Al, C-2Al and C-5Al, respectively.

2.2. Accelerated ageing test and ageing kinetics

Sintered specimens ($\varnothing$14 mm × 3 mm) were carefully polished on both sides with diamond suspensions down to 1 µm and colloidal silica to a final mirror surface. They were aged in an autoclave in steam at 160, 145, 134 and 110 °C. 3 specimens (6 exposed surfaces) were tested at each temperature and the average results were reported.

Two methods were used to determine the ageing kinetics, i.e., based on the depth of the t-m transformation propagation by μ-Raman spectroscopy or the surface t-m transformation by XRD.

2.2.1. Transformation propagation ageing kinetics (S) obtained by μ-Raman spectroscopy

Hydrothermally aged ceramic discs were perpendicularly cross-sectioned and polished, and μ-Raman spectra (SENTERRA, BrukerOptik, Ettlingen, Germany) were collected on the cross-sectioned samples to avoid the effect of the sampling depth. An Ar-ion laser source with a wavelength of 532 nm was used through a 100× objective (lateral resolution $\leqslant$1 µm) along with a pinhole aperture of 50 µm, enabling a scanning step size of 1 µm. The μ-Raman spectra integration time was 20 s with three successive measurements per point.

In order to accurately identify the m-ZrO_2 phase distribution and the stress status in the subsurface of aged 3Y-TZP, quantitative mapping (45×50 µm^2) was performed for representative ceramics, employing a scanning step size of 1 µm.

The m-ZrO_2 volume fraction was calculated according to the formula of Tabares et al. [30]:

$$V_m = \frac{I_m^{180} + I_m^{190}}{(I_m^{180} + I_m^{190}) + 0.32(I_t^{147} + I_t^{256})} \quad (1)$$

with I_m and I_t the integrated intensities of the monoclinic and tetragonal peaks respectively. The integrated intensities were quantified on background subtracted spectra using OPUS spectroscopy software.

The Raman wavenumber of the tetragonal zirconia band around 147 cm^{-1} was used to analyse the residual stress state [25] using curve-fitting software (fityk 1.2.1, Marcin Wojdyr, Warsaw, Poland) [31]. The μ-Raman wavenumber of the t-ZrO_2 peak in as-sintered stress-free 3Y-TZP ceramics was measured to be about 147.4 cm^{-1}. A peak shift towards lower wavenumbers indicates the presence of tensile stress, whereas a peak shift towards a higher wavenumber implies the presence of compressive stresses [25]. For the quantitative mappings, filled contour plots were used to visualize the transformed area and the residual stresses using a statistical software package (R3.01, R Foundation for Statistical Computing, Vienna, Austria).