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Feature article

A fast, stepwise procedure to assess time-temperature equivalence for hydrothermal ageing of zirconia-based materials

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ABSTRACT

Hydrothermal ageing is one lifetime-limiting phenomenon of zirconia-based ceramics and composites for many applications, from biomedical implants to ferrules and watches. Predicting hydrothermal ageing at use-temperature implies a set of accelerated ageing experiments conducted under water vapour at several, high temperatures (usually between 100 °C and 140 °C). From these data, the activation energy of ageing can be determined, and thus ageing can be predicted at any temperature. However, obtaining precise extrapolations with this procedure requires the use of lower temperatures (70 or 80 °C), leading to a rather long procedure (up to a few thousand hours), and should involve at least one specimen for each test temperature. This article presents a new procedure that allows the determination of all ageing parameters and the estimation of kinetics at use-temperatures with the use of a single specimen within a shorter time, accurate enough for fast screening of new materials.

1. Introduction

Zirconia ceramics can exist in three crystallographic phases at atmospheric pressure: cubic, tetragonal and monoclinic. The phase transition temperatures depend on many parameters, among which one of the most important is the nature and amount of stabilising oxides present in the ceramics. 3Y-TZP (tetragonal zirconia polycrystal stabilized with 3 mol% Y_2O_3) is the most used monolithic zirconia ceramic for biomedical applications, thanks to a combination of interesting properties: high toughness and strength (up to 6 MPa $m^{1/2}$ and 1200 MPa respectively), perfect biocompatibility, white colour and translucency. These good mechanical properties mainly come from Phase Transformation Toughening (PTT) that involves the tetragonal-to-monoclinic (t–m) phase transformation around the tip of propagating cracks, the resulting volume increase acting to close the cracks and slow them, reinforcing the material [1]. However, the same t-m transformation can occur on surfaces in contact with water, and lead to roughening and microcracking [2]. This degradation phenomenon is called hydrothermal ageing (or Low Temperature Degradation) and is responsible for the decline of 3Y-TZP components in orthopaedics in the 2000 s. To prevent it, several strategies exist. In particular alumina-toughened zirconia (ATZ) presents similar mechanical properties, while being less sensitive to ageing [3]. ZTA (standing for zirconia-toughened alumina) is also highly developed because of a higher resistance to ageing [4].

Ageing may occur at any temperature where tetragonal phase is metastable (for 3Y-TZP, anywhere below ~500 °C). Over a certain temperature range (for 3Y-TZP between room temperature and more than 150 °C) it is a thermally activated phenomenon, thus faster at high temperature and slower at low temperature. To assess ageing at room (or body) temperature, it is thus convenient to extrapolate it from experiments made at higher temperature (typically in water and in autoclave, between 80 and 150 °C). The typical procedure thus consists in measuring the evolution of monoclinic fraction with time of the surface of samples exposed to water (or steam) at different temperature, one sample being exposed to only one temperature until saturation of the monoclinic fraction. Then, from the ageing kinetics measured at (at least) two temperatures, an extrapolation to the temperature of interest can be conducted.

Any procedure to extrapolate ageing kinetics at low temperature is based on the fact that hydrothermal ageing is cumulative, and on two hypotheses:

1. Hydrothermal ageing is thermally activated in the temperature range used for the tests, thus the kinetics follow the same laws at 37 °C as at higher temperatures.
2. The ageing exponent, *n*, is constant *vs* temperature.

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If these hypotheses are satisfied, the hydrothermal ageing kinetic can be expressed as the evolution of the monoclinic volume fraction (V) *vs* time by:

$$V(t, T) = 1 - \exp\left[-(b(T)\cdot t)^n\right] \quad \text{with } b(t) = b_0 \exp\left(\frac{-Q}{RT}\right) \tag{1}$$

Thus the knowledge of the three ageing parameters b_0, n and Q allows the calculation of $V(t,T)$ for any ageing time and temperature.

The usual method [5] requires the determination of $V(t,T)$ at different temperatures, and determines analytically b_0, n and Q. Indeed, on can write Eq. (1) as:

$$\ln(1 - V(t, T)) = -(b(T)\cdot t)^n \text{ or } \ln\left(\ln\left(\frac{1}{1 - V(t, T)}\right)\right) = n\ln(b(T)) + n\ln(t) \tag{2}$$

Thus, after Eq. (2), for each temperature, plotting $\ln\left(\ln\left(\frac{1}{1-V(t,T)}\right)\right)$ *vs* $\ln(t)$ gives a straight line of slope n. Then a common value of n is chosen for all temperatures (usually the average of the values obtained at each temperature), and for each temperature a value of $b(T)$ is determined after the intercept of $\ln\left(\ln\left(\frac{1}{1-V(t,T)}\right)\right)$ *vs* $\ln(t)$ (this intercept is: $n\cdot b(T)$). Then plotting $\ln(b(T))$ *vs* $1/T$ gives again a straight line of intercept $\ln(b_0)$ and of slope $-Q/R$. This is a well-established method that gives correct results, but suffers from a few limitations that make it not always easy to use. In particular, it was shown [6] that n may vary during a same kinetic. Thus the determination of n and b may depend on the person who makes the calculations.

Another, numerical, method starts from the same data ($V(t,T)$ at different temperatures), but minimizes the global error function ε between the measured values and the ones predicted by Eq. (1) by optimizing the parameters b_0, n and Q.

$$\varepsilon = \sum_i \frac{\sum_{j=1}^{N_i}\left(1 - \exp\left[-\left(b_0 \exp\left(-\frac{Q}{RT_i}\right)\cdot t_j\right)^n\right] - f_{ij}\right)^2}{N_i} \tag{3}$$

Eq. (3) presents such an error function, in which each kinetic is given the same weight whatever the number of time points. In Eq. (3), i relates to the number of temperatures tested and j to the number of time points for each temperature (for 1 temperature T_i, N_i time points are measured); f_{ij} are the measured monoclinic fraction at temperature T_i and time t_j. Many other error functions can be used, the other most frequent one being the one in which each experimental point is given the same weight. Optimization of b_0, n and Q can be conducted numerically using a solver. This method presents the advantage to optimize all three parameters at once, and is less sensitive to measurement uncertainties. On the other hand, it must be considered with care since it will not directly reveal potential deviations from Eq. (1), contrary to the analytical method.

We propose here a new, stepwise method to extrapolate ageing kinetics to room temperature. It is based on ageing measurements at different temperature on a single sample, and can largely reduce the time necessary for correct extrapolations. In its principle it is similar to Locati procedure for the determination of mechanical fatigue limit [7], insofar as it calls on different levels of stress applied on a single sample (the "level of stress" being here a temperature) and on a "theoretical shape" of the physical quantity to characterize (fatigue limit follows a Wohler curve for Locati procedure, and here monoclinic content follows a Mehl Avrami Johnson law (Eq. (1)) for hydrothermal ageing). There are of course some differences between the method we propose here and Locati procedure. The main difference is that fatigue tests only rely on one single measurement: the number of cycles to fracture; they don't allow the evaluation of the damage parameter during the test. On the contrary, our procedure allows, and necessitates, the evaluation of the monoclinic fraction at every step of the test.

Table 1
Ageing kinetics schedules for the stepwise (SW) extrapolation procedure; Schedule SW1 and schedule SW2: all samples undergo the whole schedule; Usual schedule: three samples for each temperature.

Schedule 1: SW1		Schedule 2: SW2A, SW2S		Usual Schedule: UA, US	
T_i (°C)	Δt_i (h)	T_i (°C)	Δt_i (h)	T (°C)	Total time (h)
	0		0		0
141	4	141	4 + 2	134	150
134	3 + 4	134	3 + 4	111	650
121	15	111	15 + 20	90	3200
111	40	75	200 + 300		
100	120	90	100		
85	400	85	200		
75	1000	100	50 + 100		
		121	40 + 40		
		134	10 + 10		
TOTAL	1586		1098		4000

2. Materials and methods

2.1. Materials

Experiments were conducted on commercially available alumina-toughened zirconia balls (ceramys®, Mathys Orthopaedie, Moersdorf, Germany).

2.2. Ageing procedure

To assess the ageing procedure proposed here, hydrothermal ageing was conducted in autoclave (Wolf Sanoclav, Germany), in water vapour at different temperatures between 70 and 141 °C, according to the schedules shown in Table 1. Schedules 1 and 2 are used to apply the stepwise procedure (thus each sample is submitted to the whole schedule), whereas the Usual schedule refers to one single temperature per sample until saturation of the monoclinic fraction.

The monoclinic fractions were determined using X-Ray Diffraction (D8-Advance, Bruker, Germany) at every time point of the same schedule. XRD diagrams were acquired between 26 and 33 deg. 2θ, exposing the (−111) and (111) monoclinic peaks, and (101) tetragonal peak. The volume monoclinic fraction (f_m) was deduced from these peaks intensities using Garvie and Nicholson's equation [8] modified by Toraya [9]:

$$f_m = \frac{1.311X_m}{1 + 0.311X_m}, \text{ with } X_m = \frac{I^m_{111} + I^m_{111}}{I^m_{111} + I^m_{111} + I^t_{101}} \tag{4}$$

All ageing schedules were performed on 3 samples. All measurements of the monoclinic fraction were performed on two locations (pole and equator) of each sample.

3. Theory/calculation

3.1. Extrapolation procedures

The usual extrapolation procedures are described in the introduction. Here they are referred to as UA (usual schedule, analytical determination of the ageing parameters using Eq. (2)) and US (usual schedule, determination of the ageing parameters by global error minimisation using Eq. (3)).

The stepwise procedure presented here does not rely anymore on complete kinetics measured at different, constant temperatures. Instead, a single piece of zirconia-based material is submitted successively to different ageing temperatures. The single ageing kinetics obtained this way allows the determination of all three ageing parameters.

The method is based on a set of three equations obtained from Eq. (1), and on preliminary approach used to describe ageing at two