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Lifetime estimation of a zirconia–alumina composite for biomedical applications

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ABSTRACT

Objectives. In this work long term stability of a zirconia toughened alumina (ZTA) composite was investigated.
Methods. Accelerated aging tests under hydrothermal environment, in autoclave and hot water, at different temperature, was conducted on material sample. Tetragonal to monoclinic transformation was evaluated by XRD analysis and the monoclinic content was plot as a function of the exposure time. The kinetic of transformation was studied by means Mehl-Avrami-Johnson (MAJ) nucleation and growth model.
Results. An activation energy for tetragonal to monoclinic transformation of 99 kJ/mol was found by the Arrhenius plot of reaction rate, value in agreement with other bibliography works regarding Y-TZP and alumina-zirconia composites. The in vivo hydrothermal stability simulation, estimated by the obtained activation energy, predicts in 65 years the time necessary to reach 25 vol% of monoclinic phase.
Significance. These results support the material suitability in biomedical field, especially in dentistry applications as implantology.

1. Introduction

Yttria stabilized Tetragonal Zirconia Polycrystals (Y-TZP) were introduced as load-bearing biomaterials several years ago, with the aim to overcome the limitations in device design due to the brittle fracture mechanics of monolithic alumina [1]. The success of Y-TZP as a biomaterial was due to the combination of high fracture toughness, strength, high wear resistance and excellent biocompatibility [2]. However, it is known that Y-TZP behavior is depending on environment and condition of use. For this reason, its employ in ball heads for Total Hip Replacements (THR) has given controversial results [3] and the worldwide withdrawal of this kind of ceramic components on 2000 lead to the practical abandon of this material in orthopedics. Nowadays Y-TZP is mainly used in dentistry for fixtures, crowns and bridges, obtained by the CAD/CAM milling of blanks [4].

Mechanical behavior of polymorph zirconia is strongly dependent on the metastable nature of the tetragonal phase. The stress-induced tetragonal-to-monoclinic (t–m) transformation, in the zone ahead of a crack tip, results in increased mechanical properties by energy-dissipative mechanisms and in the inhibition of crack tip propagation [5]. Nevertheless, due to the metastable nature, tetragonal zirconia based materials are susceptible to an unfavorable phase transformation at low temperature, first reported by Kobayashi et al. [6]. The physico-chemical mechanism of the tetragonal to monoclinic

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transformation is now widely accepted and highlights the relevance of oxygen vacancies in yttria stabilized zirconia. In hydrothermal environment the water species (oxygen, hydrogen and/or hydroxyls) initially locate on oxygen vacancy sites on the material surface, due to the yttria doping. It leads to the contraction of lattice parameters, accumulation of tensile stresses in the tetragonal grains and then stress-assisted transformation [7]. The process, that starts on the surface, than progresses into the material bulk, eventually leading to the pullout of the surface grains [8].

The main consequences of LTD for Y-TZP materials are the degradation of mechanical properties and wear resistance. In view of their use as biomaterials, the kinetic of LTD should be carefully assessed because this behavior is the main limiting factor of the lifetime of zirconia-based components and may result in catastrophic failures. So far, the most promising application of zirconia as biomaterial is as reinforcement in alumina–zirconia composites [9]. The materials of this class are called zirconia toughened alumina (ZTA) when alumina is the main component, either Alumina Toughened Zirconia (ATZ), when zirconia is the main component. The benefits of alumina zirconia composite are the combination of the characteristics of alumina (high hardness, high stiffness) with the above mentioned properties of zirconia, *i.e.* the high strength and high toughness, with improvement of slow crack growth resistance [10]. In addition, several studies on alumina–zirconia composite have remarked the positive effect of alumina on the hydrothermal stability of tetragonal zirconia phase [11,12]. This is mainly due to the elastic modulus of alumina, almost twice the one of Y-TZP. Namely, the introduction of alumina increases the matrix stiffness, then the constraint that the matrix exerts on zirconia particles maintains them in the metastable tetragonal state [13], thus acting as "mechanical stabilizer". ATZ materials show improved aging resistance *vs* Y-TZP; nevertheless these composites still exhibit a certain degree of aging [14], whereas ZTA materials can exhibit much better aging resistance than monolithic Y-TZP [14,15]. Up to now, the major application of ZTAs as biomaterials is in devices for hip and knee arthroplasty, while, in our knowledge, only a few alumina–zirconia composites are commercially available as structural ceramics for dental devices [16]. During the past years, ENEA Faenza Research Laboratories developed and tested a number of compositions in the zirconia–alumina system [17] that had been showing excellent mechanical behavior joined to excellent biological safety [18,19], making them suitable for the manufacture of implantable medical devices. The aim of this paper is to evaluate, by accelerated aging tests, the resistance to the hydrothermal degradation in a ZTA material with composition zirconia/alumina 40/60 wt%, selected among the ones in above.

2. Materials and methods

Disk-shaped samples of zirconia–alumina composite (40/60 wt%) have been obtained from powders of yttria-stabilized zirconia (3YB, Tosoh, Japan), monoclinic zirconia (TZ0, Tosoh, Japan), alumina (Baikalox SM8, Baikowski Chimie, France) and chromia (Carlo Erba, Italy). The powders were wet-mixed in a Turbula mixer, using distilled water and suitable dispersant agent to form stable dispersion. The resulting stabilizer content in zirconia grains is 2 mol%. After batch preparation, cylindrical samples were obtained by uniaxial press at 60 MPa of the dry powder, followed by cold isostatic press (CIP) at 150 MPa. Pressureless sintering was carried out in air at 1550 °C.

Hydrothermal degradation tests were performed in steam and hot water, in accordance with the method proposed by Chevalier et al. [20], that allows to obtain a reasonable prediction of the increase of monoclinic fraction *in vivo* as a function of the time [21]. Before aging tests, the samples were ground and lapped with diamond paste up to 1 μm. Densities of sintered samples were determined by Archimedes method. Microstructural characterization was performed by SEM-EDS (Leo 438 VP, Leo Electron Microscopy Ltd – ISIS 300, Oxford Link) and by XRD analysis, in order to evaluate the monoclinic phase content in the ceramic materials. Diffraction patterns were collected by using Philips X-ray powder diffractometer with Bragg–Brentano geometry and Cu Kα radiation (40 kV and 35 mA). Low temperature degradation kinetics of the composite was estimated by accelerated aging tests in saturated steam in an autoclave (Vapor Matic 770/A, ASAL) at 134 °C, 121 °C and in hot water at 90 °C.

Monoclinic content was assessed according to the following equation, proposed by Toraya et al. [22]:

$$f = \frac{1.311 \times X_m}{1 + 0.311 \times X_m} \quad (1)$$

The integrated intensity ratio, X_m, was calculated using the Garvie and Nicholson method [23] as follows:

$$X_m = \frac{I_m(-1\,1\,1) + I_m(1\,1\,1)}{I_m(-1\,1\,1) + I_m(1\,1\,1) + I_t(1\,0\,1)} \quad (2)$$

where $I_m(h\,k\,l)$ is the area of the peak associated to the plane $(h\,k\,l)$ of the monoclinic phase and $I_t(h\,k\,l)$ is the area of the peak associated to the plane $(h\,k\,l)$ of the tetragonal phase.

The apparent activation energy Q was calculated by Arrhenius equation:

$$b = b_0 \times \exp\left(-\frac{Q}{RT}\right) \quad (3)$$

where b is the reaction rate, b_0 is a material constant, R is the gas constant and T is the absolute temperature. The slope of $\ln b$ plotted in function of the reciprocal of temperature gives the apparent activation energy value for phase transformation.

3. Results

The final density of the composite tested is close to 99.9% of the theoretical density (4.6 g/cm^3), calculated by the phase method.

The microstructure of the composite (Fig. 1) is characterized by equiaxial grains. The average grain size, measured by the linear intercept method according to the standard EN623-3 [24], are 0.5 μm for zirconia and 0.8 μm for alumina.