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Fracture toughness, strength and slow crack growth in a ceria stabilized zirconia–alumina nanocomposite for medical applications

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ABSTRACT

Mechanical properties and slow crack growth (SCG) behavior of a 10Ce-TZP/Al_2O_3 nanocomposite currently developed as a biomaterial are considered. Fracture toughness is determined for sharp, long (double torsion) and short (indentation) cracks and a good agreement is found between the two types of cracks. The main toughening mechanism in the nanocomposite is the tetragonal to monoclinic phase transformation of the ceria-stabilized zirconia (Ce-TZP) phase. Transformation at the surface of ground specimens leads to surface compressive induced stresses and an increase in strength. Crack velocity curves (V–K_I curves) are obtained under static and cyclic fatigue using the double torsion method. The static V–K_I curve in air reveals the three stages characteristic of stress corrosion with a threshold $K_{I0} \sim 4.5$ MPa $m^{1/2}$ and a fracture toughness of 8.8 MPa $m^{1/2}$ significantly higher than those of currently used inert bioceramics (i.e. alumina and Y-TZP). A crack growth accelerating effect is shown under cyclic loading, correlated with a decrease in the threshold. However, the cyclic fatigue threshold (4 MPa $m^{1/2}$) still stands above that of current biomedical grade alumina and zirconia.

1. Introduction

Inert bioceramics, such as alumina and yttria stabilized zirconia have been used successfully as components for orthopaedic and dental applications, due to their biocompatibility, their mechanical properties (i.e. wear resistance for orthopaedics) and aesthetics (dental restoration). Unfortunately, alumina exhibits modest strength and toughness, which limits for example, its use to standard 28 mm femoral heads and acetabular cups [1,2] in orthopaedics. Owing to the stabilizing effect of yttria (Y_2O_3) or ceria (CeO_2), tetragonal zirconia polycrystalline (TZP) ceramics can be processed. The retention of the tetragonal (t) phase at ambient temperature allows it to transform to the monoclinic (m) structure under external applied stresses. At the vicinity of a propagating crack, the stress induced transformation leads to compressive stresses that shield the crack tip from the applied stress and thus, enhances the fracture toughness [3,4]. The use of Y-TZP ceramic, especially in the 1990s, has opened the possibility to a larger range of orthopaedic implant designs. It is now widely used for dental restoration and currently developed for dental implants. However, the t → m phase transformation can also be induced at the surface of Y-TZP *in vivo*, leading to the so-called aging phenomena [5]. The aging degradation characterized by surface roughening, microcraking at the surface of the material, or particle release limits the development of yttria stabilized zirconia as a biomaterial [6]. There is therefore a need for ceramic materials with improved mechanical properties compared to alumina, and improved *in vivo* stability compared to Y-TZP.

Several zirconia–alumina composites have been recently developed to limit aging phenomena and to offer enhanced mechanical properties [7–9]. Nanocomposites, in which nanometer sized-second-phase particles are dispersed within the ceramic matrix grains and/or at the grain boundaries, have also been proposed [10,11]. They have shown significant improvement in toughness or strength. The mechanism(s) behind the improvement is (are) still in debate. Recently, Nawa et al. [12] developed a Ce-TZP/Al_2O_3 nanocomposite (with both phases being of nanometer scale) that exhibits an extremely high resistance to low-temperature degradation, a complete biocompatibility and a high wear resistance [13–15].

Here we investigate fracture toughness, strength and SCG in this 10 mol% Ce-TZP/Al_2O_3 nanocomposite. The results are discussed according to the impact of the tetragonal to monoclinic (t → m) phase transformation and residual stresses on the mechanical properties.

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2. Material and methods

2.1. Material

In this study a 10Ce-TZP/Al_2O_3 nanocomposite (Matsushita Electric works, Ltd., Kadoma, Japan) composed of 70 vol% Ce-TZP containing 10 mol% ceria, and 30 vol% Al_2O_3 was used. The details of fabrication were described elsewhere [14]. The microstructure of the composite is shown in Fig. 1. Sintered samples of the nanocomposite exhibit average grain size of 250 nm (both phases) and their preliminary mechanical properties are listed in Table 1. Samples were received as plates with dimensions $40 \times 20 \times 2\ mm^3$ for SCG measurements, and $50 \times 6 \times 4\ mm^3$ for toughness and strength measurements.

2.2. Four points bending tests

The strength was measured using a four points bending device with inner and outer spans of 10 and 35 mm, respectively. The tests were conducted at ambient air (20 °C, 35% HR) on a universal hydraulic INSTRON 8500 testing machine. The effect of compressive residual stresses on the flexural strength, 20 specimens were tested in an 'as received', ground state, and 10 specimens after annealing at 1200 °C during 12 min. It was shown previously that this treatment completely anneals residual stresses due to grinding in zirconia ceramics [16]. The specimens were loaded at high rate (5 mm/min) to avoid any slow crack growth prior to failure, and the maximum load was recorded to obtain inert strength (σ_i) distributions before and after annealing.

2.3. Stable indentation crack growth in bending tests

Fracture toughness measurements were performed using controlled indentation crack growth in bending. The procedure consists to superimpose applied bending stresses to the indentation residual stresses and to follow the crack propagation of indentation cracks. For this purpose, one sample was polished with diamond pastes down to 1 μm and three Vickers indentations were introduced applying a load of 200 N during 10 s on its tensile side (4 mm wide surface). This procedure allows obtaining three sets of data on the same sample. The indentations were centred within the inner span (10 mm) with their diagonals oriented parallel and perpendicular to the sample edges and with a distance of 1 mm apart to avoid any interaction between the cracks. The indented sample was left in air for 48 h before testing, in order to let the indentation cracks have a stable, equilibrium length. It was then stepwise loaded to increasing load levels in four point bending. The load was applied at a high speed of 6000 N/s to prevent slow crack growth during loading and subsequently unloaded at the same rate. The lengths of the three indentation cracks were then measured and the procedure was repeated until failure initiated from unstable propagation of one of them. In this study, the maximum applied load was first fixed to 200 N, and then incremented by 100 N until failure at 970 N.

During post-indentation bending, an indentation crack is subjected to a total stress intensity factor K_{tot}, given as the sum of the residual indentation stress intensity factor, K_{res}, and the applied bending contribution, K_a [17,18]:

$$K_{tot} = K_{res} + K_a = \chi P c^{-3/2} + \psi \sigma c^{1/2} \quad (1)$$

where χ and ψ are, respectively, the residual stress and crack geometry coefficients; σ is the applied bending stress and c is the surface crack length.

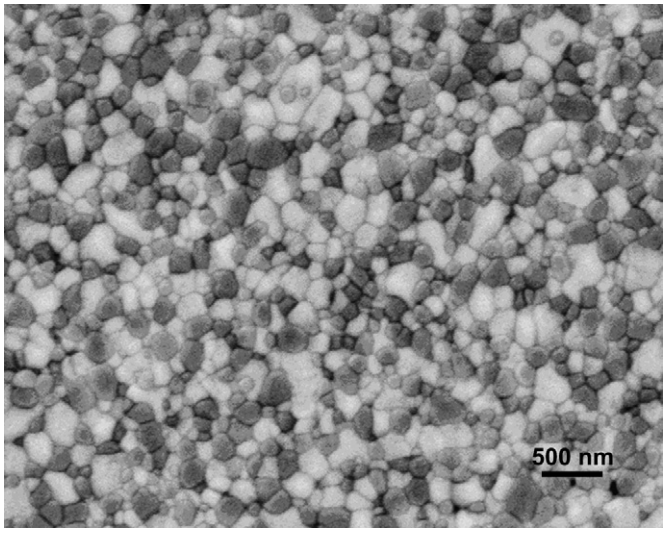

Fig. 1. Scanning electron micrograph of the nanocomposite. Alumina is the grey phase, and zirconia is in white.

Table 1
Material properties

Density (g/cm^3)	5.29
Grain size (nm)	250
Young modulus (GPa)	269
Vickers Hardness (GPa)	12

Under these fast loading conditions, crack propagation occurs when

$$K_{tot} = K_{IC} \quad (2)$$

Stable crack extension is maintained while

$$\frac{\partial K_{tot}}{\partial c} < 0 \quad (3)$$

The regime of stable crack extension (while Eq. (3) is valid), before failure when $\partial K_{tot}/\partial c \geq 0$, allows to determine crack extension curves by plotting the applied stress intensity factor $\psi \sigma c^{1/2}$ versus $Pc^{-3/2}$. The residual stress parameter, χ, and the fracture toughness K_{IC}, were obtained, respectively, from the slope and the intercept of the interpolating line considering a constant geometry factor Ψ of 1.27 corresponding to a semi-circular crack.

2.4. Double torsion tests

The double torsion (DT) method was used to determine the fracture toughness K_{IC} and V–K_I (crack growth rate versus stress intensity factor) curves, under static and cyclic loading conditions. Details of specimen geometry and loading configuration can be found in previous works [19,20]. The double torsion specimens consisted of plates of dimensions $40 \times 20 \times 2\ mm^3$, polished on the tensile surface to 1 μm finish to enable crack growth measurements. The samples were notched to 10 mm length along the center line through the full depth, using a diamond saw with 0.2 mm width, and then thermally treated at 1200 °C for 12 min. Subsequent pre-cracking was performed by loading the specimens at low rate in order to induce a sharp crack of initial length $a_i \approx 13$ mm.

To take into account the effect of the crack length on the stress intensity factor, K_I, the following expression was used for K_I calculation [19]:

$$K_I = HP\left(\frac{a}{a_0}\right)^{0.18} \quad (4)$$

where P is the applied load, H is the geometry factor in DT configuration, a is the crack length on tensile surface of the specimen, and a_0 is the notch length.

For fracture toughness measurements, the samples were loaded up to fracture at a high displacement rate of 5 mm/min and K_{IC} was determined from the maximum load.

To obtain static V–K_I curves, relaxation and constant loading tests were complementarily performed. In the relaxation test, pre-cracked specimens were rapidly loaded to a certain load value from which the displacement was kept constant. The relaxation curve (load versus time) and the crack length deduced from a compliance calibration curve were used to determine the V–K_I curve. One single relaxation test allows the determination of the entire V–K_I diagram in the velocity range 10^{-7}–10^{-2} m/s. To obtain lower crack growth rates and to investigate near threshold crack rates, a specimen was subjected to a low constant load for a duration Δt to induce a crack extension Δa and the velocity given by $\Delta a/\Delta t$, was related to the stress intensity factor. The specimen used for the relaxation test can also be used for constant loading tests so that one single specimen allows obtaining the entire V–K_I diagram from 10^{-12} to 10^{-2} m/s. The reproducibility of the results was, however, checked on several samples.

Cyclic fatigue experiments were performed under load control using a sine wave form with a ratio of minimum to maximum loads $R = P_{min}/P_{max} = 0.1$, at a frequency of 10 Hz. The maximum applied stress intensity factor, K_{Imax}, was varied so that a wide range of crack velocities was covered, with a particular interest on low applied load levels, in order to investigate the crack propagation threshold under cyclic loading. The crack growth lengths under cyclic loading were measured optically and linked to K_{Imax} to obtain V–K_{Imax} curves.

In order to evaluate the effect of environment, DT tests were conducted in air, water and in a Ringer's solution. The specimens were first sonicated in acetone then in ethyl alcohol for 5 min to insure a perfectly clean crack path. They were subsequently put in a desiccator under 10^{-2} mbar vacuum for 1 h and dropped into the testing liquid while vacuum was maintained for an additional hour. They were further transferred to the testing jig without any contact with the ambient atmosphere. This procedure insures perfect wetting of the liquid along the crack path and allows obtaining reproducible results in liquids [21].

3. Results and discussion

3.1. Strength

The strength distribution was characterized with Weibull analysis [22] which is suitable for ceramic components as their strength